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VIII. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

[Continued from p. 79.]

V.

(1) *Separation of Ice, Salt, Hydrate or Cryohydrate from Salt Solutions (continued).*

§ 148. *Separation of Ice &c. from Solutions of Chloride of Barium.*

TABLE XXIX.

BaCl ₂ per cent. by weight.	H ₂ O per cent. by weight.	Temperature at which solidi- fication begins.	Nature of solid.
5	95	— 0·9	Ice.
10	90	— 2·2	"
15	85	— 4·0	"
20	80	— 6·0	"
21·83	78·17	— 7·5	Cryohydrate.
23·98	76·02	0·0	BaCl ₂ + H ₂ O.
30	70	+ 25	"

I again found the temperature of the cryogen to be $-7^{\circ}3$ ($-7^{\circ}2$, § 78), and the temperature of the cryohydrate to be $-7^{\circ}5$ to -8° . But it is seen that as derived from a dilute solution I now find the cryohydrate to contain only 21·83 per cent. of BaCl₂, while in § 78, where it was derived from a saturated solution, I found 23·2. No doubt the smaller of these

numbers is the more correct. The composition of the cryohydrate was derived from the following data. 6.5151 of melted cryohydrate gave 1.5225. The water-worth is accordingly 41.357. The solubility at 0° C. was derived from the following :—

	1.	2.	Mean.
Solution . . .	6.7830	7.9470	
BaCl ₂ . . .	1.6214	1.9119	
Per cent. . .	23.90	24.06	23.98

§ 149. *Separation of Ice &c. from Solutions of Protosulphate of Iron.*

TABLE XXX.

FeSO ₄ per cent. by weight.	H ₂ O per cent. by weight.	Temperature at which solidi- fication begins.	Nature of solid.
5	95	-0.2	Ice.
10	90	-0.8	"
14.5	85.5	-2.0	Cryohydrate.
14.9	85.1	0.0	FeSO ₄ +7H ₂ O.

As in § 148, I find the composition of the cryohydrate to show somewhat less salt than previously (§ 82), where the cryohydrate was obtained from a saturated solution, and where the amount of salt was determined by simple evaporation. I now find the melting-point of the cryohydrate to be -2° C.; and the temperature of the cryogen is exactly the same. In the above-given determinations of the cryohydrate and of the solubility at 0° C. the solution was oxidized with nitric acid, the sesquioxide was precipitated with ammonia and weighed; the amount of FeSO₄ was thence deduced. For the cryohydrate,

4.8076 grms. gave 0.3676 Fe₂O₃, or 0.6984 Fe SO₄.

The water-worth is therefore 49.8. For the solubility at 0° C.,

7.7890 grms. gave 0.6080 Fe₂O₃, or 1.1552 Fe SO₄.

§ 150. *Separation of Ice &c. from Solutions of Tribasic Phosphate of Sodium and Hydrogen, Na₂HPO₄+2H₂O.*—This, the most usual phosphate of sodium, when used as a cryogen only reduces the temperature to $-1^{\circ}.0$ C. The cryohydrate also melts at the same temperature (I found $-0^{\circ}.9$).

Owing to this short range of temperature it is impossible to examine the separation of ice from solutions of various strengths. The determinations were made by reducing the salt to a bibasic pyrophosphate of sodium. For the cryohydrate,

	1.	2.	Mean per cent.
Solution .	6.5760	9.3401	1.72 of $\text{Na}_4\text{P}_2\text{O}_7$, or
$\text{Na}_4\text{P}_2\text{O}_7$.	0.1119	0.1627	1.83 of Na_2HPO_4 .

The water-worth is accordingly 852.

The following gave the solubility at 0°C . :—

6.7277 grms. of solution gave 0.1264 of $\text{Na}_4\text{P}_2\text{O}_7$, or 2.0 per cent. of Na_2HPO_4 .

§ 151. *Separation of Ice &c. from Solutions of Nitrate of Sodium.*

TABLE XXXI.

NaNO_3 per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	— 2	Ice.
10	90	— 4.2	"
15	85	— 6.3	"
20	80	— 8.4	"
25	75	— 10.8	"
30	70	— 13	"
35	65	— 15.5	"
40.80	59.2	— 17.5	Cryohydrate.
42.34	57.66	0	NaNO_3 or sub-cryohydrate.

There appears to be a subcryohydrate of a composition intermediate between 40.80 and 42.34 per cent. For the determination of the composition of the cryohydrate I refer to § 75. The solubility at 0°C . was derived from the data; 6.0660 of solution gave 2.5682 of NaNO_3 . It is remarkable that Marx found 44.4 per cent. and Poggiale 44.3 per cent. of the anhydrous salt. The salt I employed was made from the pure bicarbonate, and was entirely free from sulphates and chlorides. As in all similar determinations, I was not content to surround the flask containing the nitrate with ice; for I never find that by this means the temperature in the flask sinks to 0°C . A few grains of salt are added to the ice; and the temperature, as indicated by a continually agitated thermometer in the solution, remains for four or five hours at 0°C .

§ 152. *Separation of Ice &c. from Solutions of Nitrate of Lead.*

TABLE XXXII.

Pb 2(NO ₃) per cent. by weight.	H ₂ O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	-0.3	Ice.
10	90	-0.5	"
15	85	-0.7	"
20	80	-1.2	"
26.23	73.77	-2.5	Cryohydrate.
29.89	70.11	0.0	Pb 2(NO ₃).

The temperature of the cryogen is $-2^{\circ}5$. The solutions were analyzed by simple evaporation and gentle heating.

§ 153. *Separation of Ice &c. from Solutions of Nitrate of Barium.*—As the solution of this salt was found to contain only 5.37 per cent. of the anhydrous salt at 0° C., and as the cryohydrate only contains 5.3 (§ 80), only one intermediate observation on the separation of ice could be got, namely that of the 3-per-cent. solution, which gave up ice at $-0^{\circ}4$.

§ 154. *Separation of Ice &c. from Solutions of Nitrate of Strontium.*

TABLE XXXIII.

Sn 2(NO ₃) per cent. by weight.	H ₂ O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	-0.5	Ice.
10	90	-1.2	"
15	85	-2.3	"
20	80	-3.8	"
26	74	-6	Cryohydrate.
29.62	70.38	0.0	Sn 2(NO ₃).

§ 155. *Separation of Ice &c. from Solutions of Nitrate of Calcium.*

TABLE XXXIV.

Ca 2(NO ₃) per cent. by weight.	H ₂ O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	-1.1	Ice.
10	90	-2.3	"
15	85	-4.2	"
20	80	-6.5	"
25	75	-9.3	"
30	70	-12.9	"

I have not yet got the cryohydrate of nitrate of calcium.

As a cryogen it gives a temperature of -16° .

§ 156. *Separation of Ice &c. from Solutions of Acetate of Sodium.*

TABLE XXXV.

$\text{Na C}_2\text{H}_3\text{O}_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	$-\overset{\circ}{2}\cdot 2$	Ice.
10	90	$-5\cdot 1$	"
15	85	$-9\cdot 1$	"
20	80	$-14\cdot 0$	"
22	78	$-16\cdot 0$	"
23.3	76.7	$-18\cdot 0$	Cryohydrate.
26.6	73.4	$0\cdot 0$	$\text{Na C}_2\text{H}_3\text{O}_2 + ?\text{H}_2\text{O}.$

The temperature of the cryogen is exactly -18° . For the cryohydrate determination, 7.7032 grms. gave 1.7963 gm. of $\text{NaC}_2\text{H}_3\text{O}_2$. For the solubility at 0° , 4.7473 grms. gave 1.2646 of $\text{NaC}_2\text{H}_3\text{O}_2$. The water-worth is 30. The solid constituent was estimated by simple evaporation and heating to incipient fusion.

§ 157. *Separation of Ice &c. from Solutions of Acetate of Potassium.*

TABLE XXXVI.

$\text{K C}_2\text{H}_3\text{O}_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	$-\overset{\circ}{2}$	Ice.
10	90	$-4\cdot 6$	"
15	85	$-7\cdot 4$	"
20	80	$-11\cdot 2$	"
25	75	-16	"
30	70	$-22\cdot 5$	"

The solubility at 0°C . was measured both by directly weighing the dried and fused acetate, and by converting it into a nitrate by frequent treatment with nitric acid and evaporation

1.	2.
Direct.	Indirect.
6·8131 solution gave	7·4837 solution gave
4·2083 K C ₂ H ₃ O ₂ , or	4·8573 K NO ₃ , or
61·8 per cent.	62·8 per cent. K C ₂ H ₃ O ₂ .
Mean	62·3.

The cryohydrate of acetate of potassium has not yet been determined.

The temperature of the cryogen of acetate of potassium is -25° C.

It is well known that fused acetate of potassium is heavier than the anhydrous solid acetate at the same temperature ; but I do not find the remarkable fact anywhere noticed, that the fused anhydrous salt is also lighter than the aqueous solution of the salt saturated at ordinary temperatures (17° C.).

(2) *A few Organic Crystalloids in Aqueous Solution; their behaviour on being cooled and on being heated, and as Cryogens.*

§ 158. *Cane-sugar.*—Sugar-candy was finely powdered and dried at 100° C. in a current of dry air.

TABLE XXXVII.

C ₁₂ H ₂₂ O ₁₁ per cent. by weight.	H ₂ O per cent. by weight.	Temperature at which solidification begins.	Nature of solid formed.
5	95	$-0\cdot3$	Ice.
10	90	$-0\cdot5$	"
15	85	$-0\cdot9$	"
20	80	$-1\cdot3$	"
25	75	$-1\cdot8$	"
30	70	$-2\cdot4$	"
35	65	$-3\cdot2$	"
40	60	$-4\cdot1$	"
45	55	$-5\cdot4$	"
50	50	$-7\cdot0$	"
51·4	48·6	$-8\cdot5$	"
(Mean) 67·33	32·67	0·0	Cryohydrate. C ₁₂ H ₂₂ O ₁₁ .

Solutions stronger than the cryohydrate may be cooled below $-8^{\circ}\cdot5$ before solidification begins. A 60-per-cent. solution does not show signs of solidification above $-11^{\circ}\cdot4$. The solid which separates, however, is sugar. This is a consequence of the supersaturability of sugar solutions, and the

possibility of the condition of supersaturation being maintained even in solutions from which crystals of sugar are being deposited. Also, as was so notably the case with alcohol, the cryohydrate is an abundant solvent for sugar. The cryohydrate of saccharose was analyzed by evaporation.

2.2658 grms. gave 1.5244 grm. of saccharose, or 51.4.

For the solubility at 0° a solution saturated at $+20^{\circ}$ was kept for three days and nights at 0° C.

3.6300	}	gave	2.4510	of saccharose or cane-sugar.
4.1175			2.7640	

Since it will be shown in § 161 *et seq.* that the colloid forms of matter not only do not unite with water, but also do not depress the freezing-point of that liquid, it did not seem unlikely that on cooling below 0° a solution of raw sugar containing about 50 per cent. of solid matter, the solid cryohydrate would be formed and the sugar be freed from colloid impurities. As caramel certainly, and probably other foreign colouring-matters in raw sugar are colloids, I have succeeded in greatly purifying raw sugar by this method of cryohydration. Into the details of this I shall not here enter.

§ 159. *Glycerine*.—With regard to this substance a very remarkable circumstance may be noticed. That it is crystalloid we have had until lately (1) the indirect evidence depending upon its being an alcohol, and upon several alcohols being known in the solid and crystalline state, while others which are not so known yet unite with crystalline salts; (2) the direct evidence obtained from its diffusion through colloid septa. Lately it has been observed to assume the form of a crystalline solid. Again, it has lately been employed in aqueous solution in Pictet's ice-machine as a non-freezable liquid to yield heat to vaporizing sulphurous acid, and take it from water for the purpose of freezing the latter. The latter faculty of its solution to resist solidification below 0° C. proves, first, that it will form a cryogen, and, secondly, that it will form a cryohydrate—the latter fact again proving, as we shall see in § 161 *et seq.*, that it is a crystalloid.

Pure glycerine dried by being kept for a week over oil of vitriol *in vacuo*, when mixed with finely crushed ice forms a cryogen whose temperature is -19° C.

TABLE XXXVIII.

$C_3H_8O_3$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid formed.
5	95	— 0·8	Ice.
10	90	— 2·0	"
15	85	— 3·3	"
20	80	— 5·0	"
25	75	— 6·2	"
30	70	— 8·8	"
35	65	— 11·5	"
40	50	— 13·9	"
45	55	— 16·7	"

I have not yet succeeded in obtaining the cryohydrate of glycerine.

As a cryogen the glycerine behaves as hydrochloric acid and other liquid elements of cryogens; namely, the temperature obtained is lower if the liquid be previously cooled.

§ 160. *Tartaric Acid*.—As a cryogen, tartaric acid gives the temperature $-13^{\circ}5$. I cannot say that I have cleared up all the ambiguities in the behaviour of this body. The separation of ice took place with regularity as far as the following solutions are concerned.

$C_4H_6O_6$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which ice separates.
5	95	— 0·7
10	90	— 1·4
15	85	— 2·5
20	80	— 3·7
25	75	— 4·7
30	70	— 6·3
35	65	— 7·6
40	60	— 10·1
45	55	— 13

Apparently continuous with these results is the separation of a solid at $-16^{\circ}5$ from a 50-per-cent. and of a solid at $-17^{\circ}6$ from a 55-per-cent. solution. But there is here really a breach of continuity. The 55-per-cent. gives up tartaric acid at -17° when crystals of that body are introduced. And it is difficult to say whether ice, or acid, or a cryohydrate is separated from the 50-per-cent. at $-16^{\circ}5$. If a 50-per-cent.

solution be cooled to -19° and a smaller portion of the same solution which has been solidified by an ether-carbonic-acid cryogen be introduced into the first, the temperature rises to -8° , and opaque crystals are formed, while that temperature is constantly maintained. The same body at the same temperature is formed even when the first solution has only been cooled to -14° . I think, therefore, that there is with tartaric acid a body similar to that which we encountered with the iodide of sodium, namely a subcryohydrate. Owing to the sirupy nature of these strong solutions at these low temperatures, and the very slow rate at which the separation of their constituents ensues, I do not think that analyses of such intermediate subcryohydrates would be sufficiently trustworthy for reproduction. But the cryohydrate which separates at -8° is distinct enough.

4.0735 grms. of solution gave 1.8972 grm. of $C_4H_6O_6$, or 46.6 per cent.

A solution kept for two days and nights at 0° showed the following composition: 5.1304 grms. of solution gave 2.7233 grms. of $C_4H_6O_4$, or 53.0 per cent.

(3) *Colloids in aqueous solution; their behaviour on being cooled and on being heated.*

§ 161. *Generalities.*—It is perhaps only by an extension of the definition that we can regard solutions of colloids as solutions of salts. It will be of great interest to examine how far the two classes of bodies resemble, and how far they differ from one another in aqueous solution. The substantial researches of Graham on the division of matter into crystalloids and colloids, resulting as they did in the discovery of a whole series of new and profoundly interesting bodies, threw a flood of light on molecular physics. He showed that colloid septa were permeable only to crystalloid liquids, and thus established among the molecular mechanism of matter a series of connected facts similar to and of no less importance than those which have of late attracted so much attention in the domain of radiation; for that sonorous undulations are absorbed by sympathetic vibrators, that radiation is arrested by the possible authors of such radiation, cannot long be separated from the

fact that colloids arrest colloids by contact-continuity, while they are permeable (transparent, diathermanous) to crystalloids.

Recalling a few of the distinguishing properties of colloids, we find that when miscible at all with water they are miscible in all proportions. Accordingly one colloid cannot precipitate another from solution. Towards water they then behave as two gases behave towards one another. Some gelatinize (gelatine); others do not (gum-arabic). Some coagulate by heat (albumen) in association with water. In the dry state they are amorphous and show conchoidal fracture. I look upon a water-jelly as consisting of an indefinitely minute cellulation of a solid colloid enclosing liquid water. In a liquid water-colloid the solid colloid particles are present, but they do not form closed cells, and therefore do not with their contents resist change of form; nor are they necessarily in contact with one another. The viscosity of such a mass is due to friction between its solid and liquid parts. The elasticity of a jelly is due to the elasticity of its cell-walls. Thus I can form a model of a jelly by pressing together little caoutchouc bladders containing water: and in soap-suds I recognize a jelly of a higher order; that is, instead of solid we have liquid cell-walls, and instead of liquid we have gaseous contents. On heating or stirring the suds the bubbles burst, the liquid walls collapse and contract, not again to be formed automatically. On heating or stirring a jelly the solid colloid walls are broken, the liquid contents of the individual cells become continuous, so that all hydrostatic laws hold good. Let the heated liquid cool, and similar cells are restored; but on repeated heating, the cells are burst in such divers places that they are not to be restored. Such restoration is also hindered and prevented on stirring during cooling.

I gladly leave these speculations for the facts which gave them birth. Through the kindness of Mr. W. C. Roberts, F.R.S., there were placed at my disposal certain of the inorganic colloids prepared by the late Mr. T. Graham, the Master of the Mint. Some of these are spontaneously undergoing so interesting a change that I have been unwilling to disturb them. Others, notably a solution of silicic acid and of sesquioxide of iron in water, I find contain each under 1 per

cent. of oxide. I prepared, therefore, fresh solutions, following the directions given by Mr. Graham, and meanwhile examined certain organic colloids.

§ 162. *Gum arabic.*—If a 1-, 5-, 10-, 20-, 25- or 30-per-cent. aqueous solution of gum arabic be cooled, ice begins to be formed in all cases at 0° C. exactly. Even a 35-per-cent. solution, which is very viscid, begins to give up ice at 0° , and is quite solid at $-0^{\circ}5$. A 45-per-cent. solution, which is semisolid, shows a temperature of -1° at the beginning of sensible ice-formation, and is certainly solid at $-1^{\circ}2$. This very small degree below 0° C. in so viscid a substance is certainly not more than may be attributed to the overcooling of the ice already formed. I can find no trace of a cryohydrate; and that such does not exist is supported by the fact that, in spite of the great solubility of gum in water, when powdered gum and ice are mixed together the resulting temperature is 0° exactly. Gum arabic is therefore powerless as a cryogen. It is true that this might be attributed to the gum acting like a certain quantity of anhydrous chloride of calcium, which when mixed with ice may compensate, by the liberation of heat of combination, for the heat absorbed in the joint liquefaction. But that such balancing does not ensue is shown by the fact that a 45-per-cent. solution of gum also gives 0° C. with ice, while a solution, however weak, of chloride of calcium will absorb heat when liquefying ice by contact. The same is also proved by the observation that when gum is mixed with water the alteration in temperature, though certainly in the direction of heat-liberation, is very inconsiderable. In a preliminary experiment I found that powdered gum and water mixed in indefinite proportions gave a rise of $0^{\circ}75$ C. As the result of a number of more exact experiments, it appeared that the greatest heat was developed when four parts by weight of water were mixed with one of finely powdered gum arabic; a rise of $1^{\circ}1$ ensued, namely from $15^{\circ}7$ to $16^{\circ}8$. The first temperature was that of the water in the outer of two concentric beakers, the inner of which contained the gum. The beakers were thickly wrapped and covered with flannel, and had been in such contact for several hours. To the above numbers, however, I do not attach much quantitative value; for, owing to viscosity, solution takes place very

slowly. The results, however, clearly show that the heat developed is far too small to counteract any great heat-absorption by solution, and that accordingly the latter does not exist. The heat liberated is indeed scarcely more than the heat of capillarity.

I believe that most of us would have been disposed to predict that in order to boil a solution of gum a temperature above 100° C. would be required. This was, I confess, my own persuasion until I was enlightened by the above experiments on the separation of water as ice from gum-solutions of all strengths. But being so enlightened I was able to predict that a solution of gum would boil at a temperature not above 100° C. A 20-per-cent. solution of gum arabic appeared to boil in a test-tube over the bare flame below 100° C. But as it is almost impossible to avoid a certain amount of decomposition under these circumstances, a tube holding a fresh quantity of the 20-per-cent. solution was placed in a wider tube containing a solution of chloride of sodium which boiled at 104° C. On heating the latter gradually the gum-solution could be made to boil before the brine began to do so. And if by rapid heating the latter were made to boil, the gum-solution boiled violently, and continued to do so after the brine had ceased. A thermometer in the gum-solution showed 100° C. Further, a 40-per-cent. solution of gum arabic when surrounded by boiling water boils at 98° C., or two degrees lower than the water.

§ 163. *Albumen*.—Dry albumen when mixed with ice can only depress the temperature $0^{\circ}\cdot 25$ C. Four parts by weight of water and one of albumen, both at $18^{\circ}\cdot 2$, gave, on mixture, a temperature of $19^{\circ}\cdot 5$. In another experiment the common temperature rose from 19° to 21° . In the above experiments commercial albumen was used. For more exact experiments white of egg was used, which analysis showed consisted of 13·37 per cent. of albumen (dried at 100° C.) and 86·63 of water. Such white of egg begins to separate ice at 0° C., and freezes into a solid mass at $-0^{\circ}\cdot 5$. A solution diluted to 5 per cent. begins to give up ice at 0° C., and is solid at $-0^{\circ}\cdot 2$ C. A 10-per-cent. solution separates ice at 0° C., and forms a solid mass at $-0^{\circ}\cdot 3$ C. The boiling-points of albumenoid solutions, of course, could not be determined. And

the addition of alkalis to prevent coagulation would naturally vitiate the results.

§ 164. *Gelatine*.—The gelatine used in the following experiments was such as is commonly used by confectioners. Solutions of this substance containing 5, 10, 15 and 20 per cent. may be rapidly cooled under constant stirring without gelatinization. Ice in all such cases begins to be formed at 0° C.; and the whole becomes solid at that temperature. Stronger solutions are so difficult to manipulate, on account of their gelatinization and consequent hardness, that the results with them are doubtful. As far as the experiments extend, however, they fail to show that the freezing-temperature is affected.

A 20-per-cent. solution heated (as in § 162) in a brine-bath boiled at $99^{\circ}\cdot 9$ C. A 45-per-cent. solution boiled at $97^{\circ}\cdot 5$; and a 50-per-cent. solution, which is as stiff as the strongest glue used by cabinet makers, boiled also at $97^{\circ}\cdot 5$. A very striking and conclusive experiment is, to surround the tube containing the 50-per-cent. solution with distilled water in another tube. If the exterior water-tube be heated slowly, the glue in the inner tube boils before the water in the outer one. On continually stirring the frothy viscid mass, the true boiling-point is observed to be constant at $97^{\circ}\cdot 5$.

As an experiment the above is exceedingly instructive, and, I believe, novel; but, like so many novel and instructive phenomena, it is one of daily occurrence. The blistering and frothing of the strongest glue when heated by steam or water in the outer pot has certainly been observed hundreds of times in every carpenter's shop. Is it strange or is it natural that so familiar a fact should never have struck us as requiring explanation?

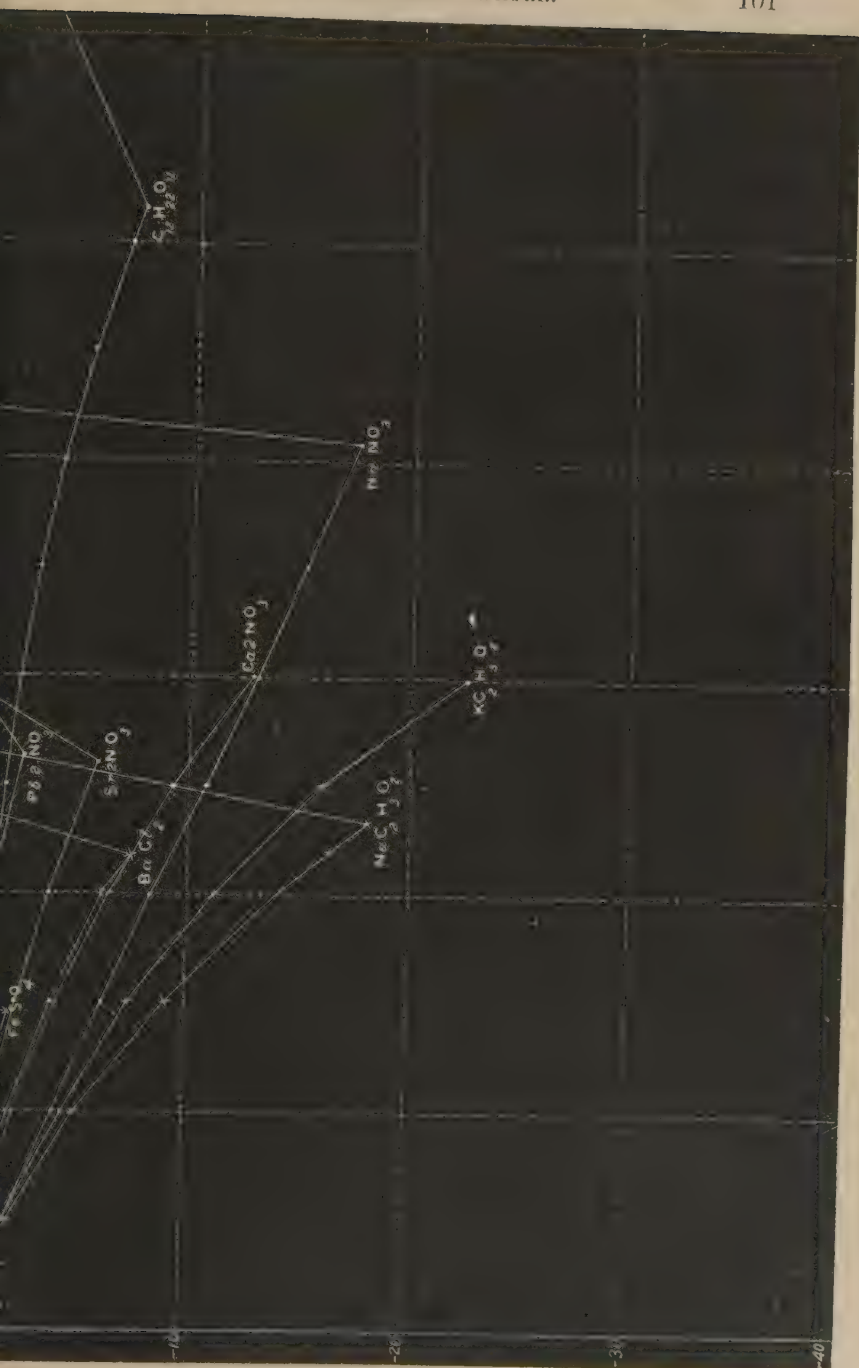
§ 165. *Mixtures of organic colloids*.—To round off the series of experiments with colloids homologous with those of crystalloids, I next examined a mixture of gum arabic and gelatine. A solution was made containing 20 per cent. of gelatine, 20 of gum arabic, and 60 of water. This began to freeze and froze completely at 0° C. It boiled at $97^{\circ}\cdot 7$ C.

(4) *General remarks on colloids*.

§ 166. The depression of the boiling-point of water by the solution in it of organic colloids has its analogies. Amongst the

metals innumerable instances occur to us in which the melting-point of an alloy is not only lower than that of one constituent, not only lower than the mean of the two, but lower than that of either or any of the constituents—witness the “fusible metals.” When metals are alike in chemical affinities, they have little affinity for one another. They mix mainly by diffusion. They dilute one another. If we mix sodium with sodium, we certainly dilute each sodium with the other; the adhesion which we supply is exactly equal to the cohesion which we replace; the resulting mass is identical with its constituents. But if we mix potassium and sodium together, by diffusion we diminish cohesion, and the adhesion introduced is less than sufficient to replace it; from two solids we get a liquid. The similarity of the metals prevents their having any notable relationship with one another. Equally to the purpose is the recollection of the alteration in boiling-point which follows the mixture of liquids which are chemically neutral to one another. Many a month has been wasted in the attempt to get propylic alcohol from fusel oil, owing to the fact that a mixture of amylic and butylic alcohols will commence to boil at a temperature below the boiling-point of butylic alcohol. Moist ether boils below dry ether; and even a liquid such as iodide of ethyl, which is almost insoluble in water and which dissolves but little of that body, has its initial boiling-point already lower than that of water. The work done by the heat in separating the particles of a body is already effected by the interpenetration of the associated body. Cohesion is diminished and a less heat-tension is required to complete the separation of the more volatile constituent as vapour.

From another aspect we may consider the neutral body to act as an infinite series of points, and recall the fact that, on evaporating saturated solutions of various salts over a steam-bath, bubbles are frequently formed beneath the salt-pellicle, owing perhaps to the multiplicity of points, at temperatures certainly below 100° C., while the clear solution of the same salt when saturated demands a temperature several degrees above 100° C. for ebullition. The rise in temperature shown on mixing a dry colloid with water is probably connected with the deficit below 100° C. of the temperature required to boil the resulting colloid solution.



Returning to the separation of ice from colloid solutions, we must conceive that when ice so separates that the solution becomes enriched in regard to the colloid body, the particles of ice in contact with the source of cold become overcooled (that is, fall below $0^{\circ}\text{C}.$) on account of the insufficient circulation and the imperfect thermal conductivity of ice and of the colloid solution. But when such over-cooled ice is stirred with the colloid solution a fresh portion of ice is formed if the latter is already at $0^{\circ}\text{C}.$; if above $0^{\circ}\text{C}.$, then some of the ice melts: in either case the $0^{\circ}\text{C}.$ is restored. Ultimately the solid particles of the anhydrous colloid must lie side by side with the ice particles, as they do when the two are mixed as powders, as in § 162. They are as independent of one another as are the particles of ether and chloroform when the two are mixed, or as are the particles of two gases which diffuse through one another without combination.

I reserve the results which I have obtained with inorganic colloids for a future communication.

The figure shows the same constants as were shown in the figure, Paper IV., but with the new salts.

IX. *On some Phenomena of Induced Electric Sparks.*

By S. P. THOMPSON, B.A., B.Sc.

[With a Plate.]

1. THE observations communicated in this paper are the result of an investigation into the phenomena discovered in November 1875, in Newark, N. J., by Messrs. T. A. Edison and C. Batchelor, and alleged to demonstrate the existence of a new form of energy. A detailed memoir of the phenomena has since appeared in the 'Quarterly Journal of Science'*, by Dr. G. M. Beard, of New York, who accepts, with some hesitation, the hypothesis of a new force.

2. When a galvanic current passing through the coils of an electromagnet is rapidly interrupted, minute bright sparks can, at the moment of interruption, be drawn from the electromagnet-core by an earth-wire or by any conducting substance

* "The newly-discovered Force," by George M. Beard, A.M., M.D., New York (Quarterly Journal of Science, No. L. April 1876).

Fig. 1.

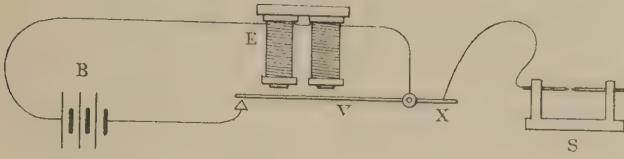


Fig. 2.

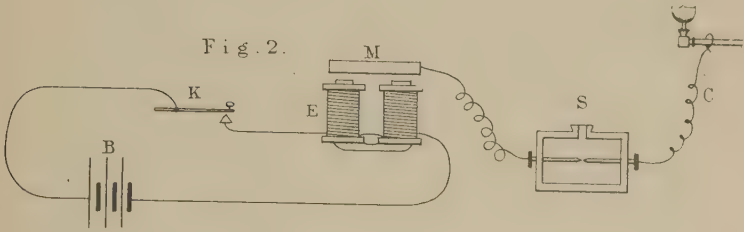


Fig. 3.

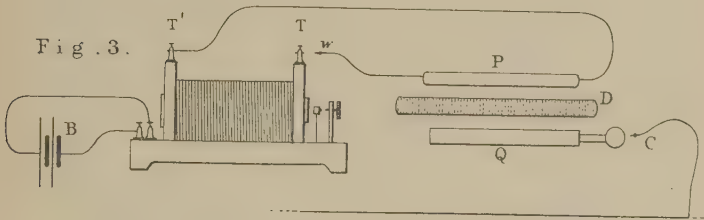


Fig. 4.

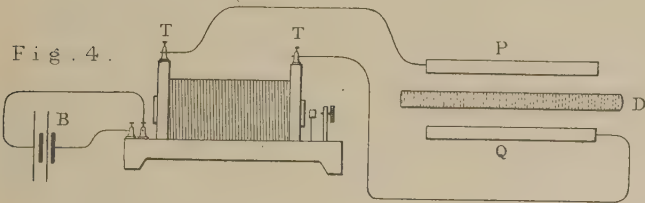
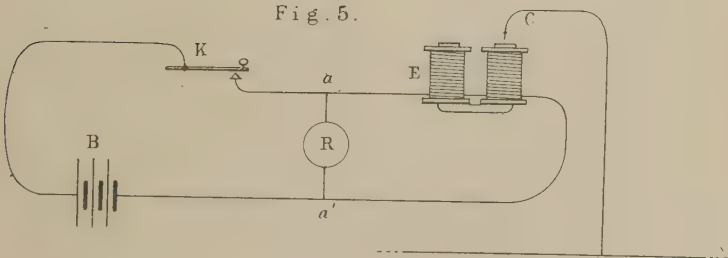


Fig. 5.



held in the hand and presented to the core*. These sparks are best seen when the electromagnet-coils, interrupter, and battery-cells are completely insulated from the ground. The substitution of a bar of any metallic substance, or even carbon or wood coated with tinfoil, in place of the iron core of the electromagnet, does not prevent the production of the spark. With bars of zinc or cadmium, or, better still, of either of these metals amalgamated on the surface, the sparks are brighter.

The minuteness of the sparks makes observation of them a matter of some difficulty; between two points of graphite pencils in a dark box they are more readily seen. They are conducted by all metallic bodies, and by the body; and even pass into insulated conductors of large surface, apparently requiring no completion of the circuit. This circumstance, however, as well as the supposed inability of the sparks to produce any indications upon the galvanometers and electroscopes of ordinary use, may be explained by a further knowledge of their nature. It was this apparent lack of polarity in the nature of the discharge that led to the adoption of the hypothesis of a new form of energy; and the assumption seemed further to be borne out by an apparent absence of physiological effect.

Two forms of the apparatus at first employed to produce the sparks in question are given in figs. 1 & 2. In the first case, where the circuit was rapidly interrupted by an automatic vibrator, the sparks were drawn from the electromagnet-core or from the vibrating armature. In the second they were drawn from a bar of metal placed above, but not in contact with, an electromagnet in a circuit completed by a depressor key.

3. Careful repetition of the experiments failed to elicit evidence of polarity in the spark, or to procure response to

* As an interrupter almost any form will answer; a Morse key is good for slow interruptions by hand; or an automatic vibrator, similar to the "break" of an induction-coil may be employed. Similar sparks have doubtless been often noticed by those who have used any form of apparatus involving rapid interruption of the current, and as often attributed to defective insulation. The writer of this paper observed the same thing some years ago in a trembler of particularly good construction, and in vain rewound the coils in hope of eliminating the supposed leak.

the ordinary electrical tests. And the wish to obtain further information upon the nature of this peculiar discharge by studying its effects in illuminating the rarefied gases of vacuum-tubes, rendered it necessary to seek a means of more plentiful production, and to abandon the methods of the original investigators already described; for the sparks so obtained had never exceeded the quarter of a millimetre in length, and were quite incapable of producing a luminous discharge through a small vacuum-tube.

The following experiments led to the method desired:—

A rod of soft iron 20 centims. in length was wrapped in folds of vulcanized sheet rubber to a thickness of 2 centims. Around the exterior of this 150 centims. of stoutly insulated copper wire were wound. One end of this wire was connected with one terminal of the secondary wire of a small induction-coil *, the other end was brought within 15 millims. of the other terminal. The intent of this arrangement was to pass, as in the previous experiments, an intermittent current around a metallic conductor. When the coil was set in action the secondary currents passed with rapid discharge across the interval of about 15 millims. between the end of the wire and the terminal; and it was then found that sparks of several millimetres length could be drawn from the iron rod within the folds of vulcanized rubber by an earth-wire, or by the finger, or by any conductor held in the hand. It was found impossible to convey any charge from the iron rod by a proof-plane to an electroscope; and on leading a wire to a sensitive long-coil galvanometer by Colladon no deflection was obtained, though the sparks were drawn from the wire beyond the galvanometer, through which the force thus manifesting itself must therefore have passed. Identical effects followed the substitution of bars of copper, cadmium, and zinc for the iron rod.

It was next ascertained that no perceptible difference of potential existed between the two ends of the metal rod, and none between the ends and the median portion. The spark

* This coil, capable of throwing sparks of 50 millims. length with two cells of Grove's element, was employed in most of the succeeding experiments. Each piece of apparatus used, including the cells of the battery, was carefully insulated from the table.

could be drawn indifferently at either end, or at the middle, but not from two points at once; nor could it be led by an insulated wire from one point of the bar to another. Other metallic objects in the neighbourhood of the bar became similarly affected; and from them sparks could be drawn. These effects were augmented when the distance of 15 millims. over which the secondary current of the coil discharged itself as a spark was increased to 20 millims. They diminished when the distance was reduced to 5 millims., and ceased entirely when the interval was reduced to nothing, so that the secondary current of the coil passed along unbroken metallic connexions. The conclusion to which these results pointed was apparently that the effect was one of surface-charge. This surmise might be directly tested by increasing the size of the metallic core and the number of surrounding turns of wire.

4. The arrangement next to be described*, and shown in diagram at fig. 3, was therefore directly suggested by the preceding experiments. It remained practically unchanged in the subsequent investigation. A large Leyden jar was taken and its inner and outer surfaces joined by a metallic wire, constituting it simply a conductor of large surface. Around it were wrapped sheets of vulcanized rubber to a thickness of 25 millims. About this again were coiled about 30 metres of stoutly insulated copper wire†. As before, one end of this wire was led to the terminal T' (fig. 3)—the other

* It will be plain, from the subsequent details, that this arrangement plays the part of an accumulator or condenser, the interior surface of which is represented by the Leyden jar, the exterior being represented by the wire coiled outside. A Leyden jar is not essential; any cylindrical conductor is as good if of large surface; and a sheet of tin-foil laid upon the exterior of the insulating material is more effective than 50 metres of covered wire wound round it. The precise form of the accumulator is immaterial; but thorough insulation must be secured. The above arrangement is preferred because its parts are analogues of those of the experiments that suggested it. The knob of the jar is moreover convenient for drawing sparks from.

† To avoid confusion, in fig. 3 the condenser arrangement is given in diagram, D standing for the insulating folds of rubber, P for one condensing surface (the external wire coils), Q for the other condensing surface (the Leyden jar, which acts in this combination as if made of one piece of metal).

end, w , being placed near the terminal T, and so adjusted that the distance w T might be increased or diminished at will.

5. When the coil was set in action, sparks could be drawn by an earth-wire, C, from the knob of the accumulator, Q. When the discharging-distance of the coil w T was less than 5 millims., the sparks drawn from Q were minute, not exceeding 1 millim. in length, destitute of perceptible physiological action, producing no deflection when led through an ordinary needle-galvanometer, and, as before, were incapable of imparting any charge to a proof-plane.

When w was removed to a distance of 10 millims. from T the sparks at Q were larger and brighter; when the distance was increased to 20, 25, and 30 millims. successively, the sparks drawn at Q were much more vivid and exceeded 10 millims. in length. These sparks, though producing comparatively little effect in contracting the muscles of the arm, were excessively painful and penetrating to the nerves of the skin. Their light was brightest when they passed between poles of zinc, mercury, or carbon. Their brilliance was augmented and their length was increased to above 20 millims. when w was withdrawn so far from T that only a faint brush discharge passed across from w to T, a distance of about 50 millims.; and a still greater effect was produced when T was directly connected with earth. This modification virtually changed the arrangement to that indicated in fig. 4*.

6. When the spark obtained between Q and the earth-wire C exceeds 4 millims. in length, it is capable of illuminating a small vacuum-tube. The illumination differs, however, in a remarkable manner from that produced by the ordinary direct discharge of the induction-coil. Instead of the usual phenomena of a small brush of light at the positive pole, and a

* Since the communication of these experiments to the Physical Society, my attention has been called to an article in the Journal of the Franklin Institute for June 1871, by Prof. E. J. Houston, of Philadelphia, where, under the title of "A New Connexion for the Induction-coil," he describes a somewhat similar arrangement, in which an insulated conductor is employed in connexion with the coil. With this combination Prof. Houston observed some curious effects of induction in neighbouring bodies; but he seems to have thought them due to escape of electricity, and apparently had no suspicion of the real nature of the sparks so produced.

bright aureole or glow surrounding the negative pole, the illumination is symmetrical, alike at each pole, having both brush and glow at each, and is unaltered by reversing the primary circuit of the coil. An occasional flash, however, seemed to glow at one pole or at the other.

On making single contacts by holding the break-piece of the induction-coil in the fingers the effect was as follows:— at each make-of-contact no illumination; at each break-of-contact an illumination of the same symmetrical nature, affording no evidence of polarity of discharge in one direction more than in another.

7. To ascertain whether the discharge at the two poles was simultaneous or alternating, a rotating mirror was placed beside the vacuum-tube. The images were found to be, roughly speaking, alternate, the discharges being alternately from either pole. The irregularity of the alternation appeared to be dependent partly upon the distribution of the resistances in the circuit, partly upon the irregularities in the vibrations of the break. The occasional flashes of light at one pole or the other were explained by the occasional appearance in the mirror of two contiguous images having the same position, indicating the occurrence of two consecutive discharges in the same direction.

With rotating slits the same phenomenon of reciprocating discharge was observed, though less advantageously.

8. One terminal of a long-coil Thomson's reflecting galvanometer, by Elliott Bros., was put to earth, the other being connected with Q (fig. 3). When the distance wT was less than 5 millims. no deflection was produced upon the needle and mirror, a tremor being the only result. But when the distance wT was gradually increased, and the secondary discharge had consequently to accumulate upon its conductors to acquire sufficient density to overleap the resistance of the increased thickness of air between w and T , the tremulous motion of the galvanometer-needle became much more marked, the spot of light wandering about on either side the zero of the scale, never at rest, but showing no permanent deflection. When the distance wT was increased to nearly 50 millims. the brisk flow of sparks gave place to the brush discharge, varied only by the passage of an occasional spark. In this

case the wanderings of the spot of light on the scale were still more exaggerated, the needle apparently being turned little by little with an increasing deflection during some twenty or thirty vibrations of the contact-breaker of the coil, then receiving a sudden impetus in the opposite direction as the secondary spark discharged across the interval wT . This result was entirely confirmatory of the occasional flashes previously observed in the vacuum-tube, with which, on further examination, the more violent oscillations of the galvanometer-needle were found to be simultaneous. The experiment also accords with the previous observations of physicists with respect to the oscillations of the induced currents of the coil. It explains, too, why with an ordinary needle-galvanometer no deflection had been obtained with the minute sparks yielded by the earlier experiments.

9. Having again diminished the distance wT to 5 millims., a wire was led from Q to the knob of a gold-leaf electroscope. No divergence of the leaves took place; but on drawing sparks by the hand or by an earth-wire from the electroscope knob, from Q , or even from T' , a divergence of the leaves took place, rapidly followed by collapse at every spark so drawn, the gold leaves being thrown into a state of violent flutter. If the hand, or earth-wire, were suddenly removed from contact, a residual charge usually remained upon the leaves of the electroscope; and this charge was variously positive or negative, changing sign apparently according to the last oscillation of the secondary discharge.

Experimentation with the electroscope could not be carried on when w was removed more than 10 or 12 millims. from T , as the momentary charges received by the gold leaves were so violent as to destroy them.

10. Throughout the above experiments the most curious effects of induction were exhibited by all metallic bodies in the neighbourhood of the apparatus. From any of these within a range of several yards sparks of a similar reciprocating nature could be drawn by bringing near an earth-wire or any conductor of large surface, whether insulated or not.

11. It was found, as in a preceding case stated at the close of § 3, that no sparks could be drawn from Q (fig. 3) when w was brought up to actual contact with T . That is, an in-

termittent current (as is that in the secondary wire of the coil) passing through a *closed* circuit does not evoke that kind of disturbance in a neighbouring conductor which is evoked when the intermittent current has to overleap an interval of air, however short. This result proved that the appearance of a momentary charge upon Q when *w* and T were separated was the result of induction from a momentary charge upon P, and not merely from a current passing through P. The well-known phenomenon of the statical charge produced upon the separated terminals of the secondary circuit of an induction-coil will account for the presence of single momentary charges upon P and upon T. These charges must accumulate through a short but definite period of time until they have acquired sufficient density to overleap with a spark the resistance offered by the layer of air *w* T—the density of the accumulating charge depending on the dryness of the atmosphere, the perfectness of the insulation, and the distance between *w* and T. Though this period be very short, such charges will necessarily, by the inductive influence of their presence, disturb the electrical equilibrium of all near conductors such as Q. The equally well-known phenomenon of the return-stroke, investigated by Lord Mahon in 1779, will account for the appearance of a return-spark after an interval perhaps not exceeding the thousandth part of a second, thus establishing the reciprocating nature of the discharges passing between Q and C.

12. In the case of the earlier experiments (§ 2), where an interrupted primary current passes round an electromagnet, similar conditions virtually exist. The extra-current consequent on breaking the primary is a current of high electromotive force, like the secondary current of the coil. It, too, has a sensible interval to overleap, though the distance in this case is not constant. It, too, must accumulate upon its conductor in order to acquire sufficient density to overleap the gap in the circuit. It, too, can therefore, during a distinct minute period of time, analyze the neutral electricity of the electromagnet-core across the dielectric of silk or cotton that insulates the conducting wire therefrom. In this case, too, we have consequently the conditions of a rapidly charged and discharged condenser, giving rise to reciprocating induced sparks.

13. This conclusion can be directly proved by recurring to the earlier experiments (fig. 2) and introducing across the circuit a wire of suitable resistance to short-circuit the extra-current so that it may complete its route without having to overleap the break at the key. This is shown in diagram in fig. 6, where R is a box of resistance-coils introduced between a and a' . If the wire of which the electromagnet E is made be stout, its resistance will be a mere trifle, and a resistance of 3 or 4 ohms at R will be sufficient. In some cases a drop of pure water between the points of contact at K has also the result of obviating the extra-current spark. And in every case, when the conditions are so arranged as to obviate the appearance, on breaking contact, of the extra-current spark at K, no earth-wire, nor any conductor, will draw a spark from the electromagnet-core—a decisive proof that the sparks so drawn were due to induction by the statical charge of the accumulating extra-current, and to that alone.

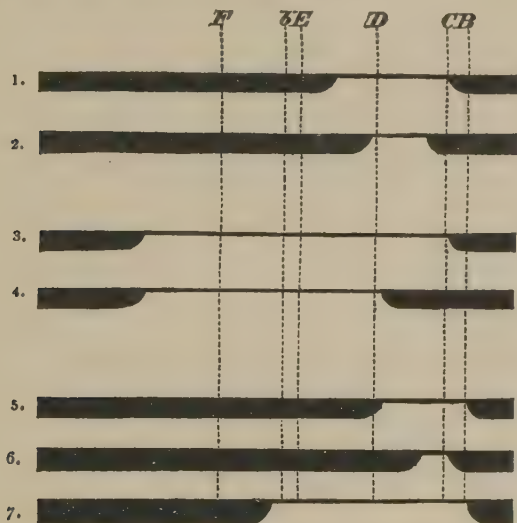
VIII. *Selective Absorption.* By WILLIAM ACKROYD.

AT present much attention is being paid to absorption-spectra for technological as well as purely scientific reasons; but in the absence of classification and of a general theory accounting for the facts observed, the whole subject is surrounded by a haze which it were well for progress to dispel. Much perplexity and not a few mistakes have arisen from the confusing of two kinds of absorption, or at least two different manifestations of the same phenomenon, which hitherto have not been sufficiently contradistinguished. These we propose to classify on the basis of the following typical experiments.

1. Light is transmitted through a thin layer of potassic dichromate at the normal temperature, and again at a little below its fusing-point. We obtain spectra approximately represented by Nos. 1 & 2. It will presently be shown that this increase of absorption at the higher temperature is the result of structural alterations in the dichromate. We shall therefore call this kind of absorption *structural absorption*.

2. A glass cell, 15 centims. \times 3 centims., contains cupric

sulphate in solution. Light sent through the 3-centims. direction gives spectrum No. 3, whilst light transmitted through the 15-centims. direction gives spectrum No 4. We have here increase of absorption without any structural alterations in the absorbing medium; for the cupric sulphate remains the same during the two observations, and the temperature is unaltered. The only difference is one of extent of medium. For this kind of absorption we propose, at the suggestion of Dr. Guthrie, the term *transverse* absorption.



Professor Gladstone*, when speaking of the action of heat on coloured solutions, thus tacitly refers to the two kinds of absorption:—"The elevation of temperature seems merely to heighten the absorbent power of the dissolved salt, so that light absorbed by a certain quantity of the heated solution is the same as would have been absorbed by a larger quantity of the same solution if cold." Notwithstanding this, the two kinds of absorption seem not to have been formally separated; and the mixed inferences from one and the other have naturally produced a confusion in the minds of students which has made selective absorption a subject little understood. We shall confine our observations to structural absorption.

* Phil. Mag. [IV.] vol. xiv. p. 423.

Structural Absorption.—Alteration of structural absorption upon elevation of temperature is, as a rule, obvious to the eye as a change of colour. This colour-change, for which I have elsewhere proposed the name of metachromatism, has been studied by Schönbein, Gladstone, Houston and Thompson, and, lastly, by myself. Many theories have been offered to account for the phenomenon; these were discussed in my paper on Metachromatism*, read before the Chemical Society on the 3rd of February last.

If a little oxide of zinc be heated strongly on a piece of white porcelain, it changes from white to orange and yellow. Chromate of lead treated similarly changes from orange to deep orange, brick-red, and black-red. These bodies quickly regain their original colour with a return of the normal temperature; hence one might suppose that the chromate of lead, if cooled far below the normal temperature, would acquire in succession the yellow and white of the zinc oxide, thus (in the order of cooling)—black-red, brick-red, deep orange, orange, yellow, and white.

Such a sequence of colour-change is exhibited by nitric peroxide; a ruddy vapour at the normal temperature, it becomes orange, yellow, and below zero a colourless liquid. From a study of such metachromatic facts and their sequence we have arrived at the following scale of change:—

<i>Metachromatic Scale.</i>		
Heating or expanding.	↑	Black
		Brown
		Red
		Orange
		Yellow
		Green
		Blue
		{ White or
		{ Colourless.
	↓	
		Cooling or contracting.

The scale may be illustrated by heating the following anhydrous bodies on white porcelain. Zinc oxide changes from white to yellow and orange; metaborate of copper from blue to green and yellowish green; baric chromate from yellow to orange; mercuric oxide from orange-yellow to orange, red,

* Chemical News, vol. xxxiv. pp. 76, 77.

and brown ; potassic dichromate, red to dark red ; trimanganic tetroxide, reddish brown to nearly black ; and cuprous oxide glass from scarlet to dark scarlet and black.

Respecting this colour-change, we make out:—(1) that it arises from increased structural absorption with elevation of temperature, the more refrangible increment increasing at a greater rate than the less refrangible ; and (2) that the only necessary concomitant is alteration of atomic potentiality—a change from the white towards the black end of the meta-chromatic scale signifying atomic recession, and a change from the black towards the white end, atomic approach.

(1) In support of this we must refer to the bichromate experiment. The change from red to dark red viewed spectroscopically gives spectra Nos. 1 and 2.

(2) To arrive at the approximate cause, I have heated colour-changing bodies in various media, as nitrogen, carbonic anhydride, and hydrogen, the result of which has been to show that the surrounding medium has nothing to do with metachromatism. The phenomenon is exhibited by all three states of matter—by solids (amorphous and crystalline), by liquids, and by gases near their liquefying-points. By a process of elimination it may readily be seen that the phenomenon is due to the reception of energy from the heating agent. Now of this transferred kinetic energy a portion is converted into energy of position. In the metachrome or colour-changing body we have therefore—

i. Kinetic energy, and the complementary.

ii. Potential energy. This energy of position is acquired by

α. The overcoming of cohesion (molecular recession or molar expansion), as, *e. g.*, in the conversion of ice into water, and water into steam, *work which is accompanied by a change of density.*

β. The overcoming of chemical attraction (atomic recession or molecular expansion), which finally ends in decomposition, as, *e. g.*, in the resolution of PtCl_4 into PtCl_2 and Cl_2 .

I. Now metachromatism is not confined to the coloured bodies one meets with in the laboratory ; for many anhydrous silicates exhibit colour-change, and in some the change is permanent after the metachrome has been subjected to a high

temperature. *This is shown in the following Table* in each example save that of olivine.

Density before ignition.		After ignition.
1. Olivine	Pistachio-green .. 3.389	Pist.-green .. 3.378
2. Beryl.....	Straw-yellow 2.697	Blue 2.697
3. Topaz	Sherry 3.539	Pink..... 3.533
4. Zircon	Brown 4.515	White 4.540
5. „	Aurora-red 4.863	Colourless .. 4.863

If we might assume that *two bodies of identical chemical composition and density* have at a common temperature the same amount of kinetic energy, then it is evident that we may eliminate kinetic energy from the list of possible causes. For, to take the beryl (2), we have differences of colour (that is, of structural absorption) at a common temperature, and the same in the zircon 5, without alterations of density or chemical composition.

The behaviour of mercuric iodide is perhaps a less equivocal demonstration of this point. Examined spectroscopically at (say) 16° C., a band of red light is transmitted extending from B to D. This narrows as the temperature rises (in other words, there is an increase of structural absorption), up to about 140° C. The band of transmitted light now suddenly widens and extends to a little beyond *b*. Spectra Nos. 5, 6, and 7 illustrate this change. After the decrease of absorption as represented by No. 7, we have the normal increase with elevation of temperature; but still at 220° C. there is not so much light absorbed as there was at 16° C. Now the heat or kinetic energy of a body increases with elevation of temperature; therefore the deep orange HgI_2 at 220° C. has more kinetic energy than the red modification at 16° C.; but the latter has greater structural absorption. The rule is that increase of kinetic energy is accompanied by increased structural absorption. In the behaviour of mercuric iodide we have the opposite of this, viz. decrease of absorption with increase of kinetic energy, whence we infer that the change of absorption which characterizes metachromatism is not necessarily accompanied by change of kinetic energy.

II. Expansion by heat (*i. e.* decrease of density) is an all

* Compiled from "Some Experiments on the Density of Garnet, &c." (Church), Chem. Soc. Journ. vol. xvii. pp. 386 & 415.

but universal law so far as we at present know. There are several exceptions, however; and many of these are among the silicates. Their anomalous behaviour is, as a rule, pointed out by the colour-change, as in the case of the zircon. But there may be change of colour, as in the beryl, without alteration of density, *i. e.* without appreciable molecular approach or recession. On the other hand, we have in olivine an example of change of density (molecular recession) without a corresponding alteration of colour. More facts of the same nature might readily be adduced, from which we infer that molar expansion or contraction is not a necessary concomitant of alteration of structural absorption. We have now excluded from our list of possible concomitants i. and ii α . Hence it would appear that ii β is the only necessary concomitant—a conclusion which receives strength when we consider that the gradual increase of structural absorption in such bodies as HgO , PtCl_4 , and $\text{Cr}_2\text{O}_5\text{Ko}_2$ terminates with their resolution into lower compounds, or into their constituent elements.

Relation of Colour to Density.—An attempt was made in 1765 by Delaval to show the connexion between colour and density. In a paper read before the Royal Society, he observes* :—"It appears from Newton's experiments that denser substances ought by their greater reflective power, in like circumstances, to reflect the less refrangible rays, and that substances of less density should reflect rays proportionably more refrangible and thereby appear of several colours in the order of their density." The seeming success of this attempt is perhaps due to the comparative nature of his facts; for he compares coloured glasses of each of the following metals in the order of their densities:—gold, red; lead, orange; silver, yellow; copper, green; iron, blue. We can readily see now the error of such a comparison; for the colour of glass must evidently depend upon the state of the metal in it; *e. g.* differently coloured glasses may be obtained from the different oxides of the same metal. To take an instance, whilst the cupric oxide gives a bluish-green glass, we know that the cuprous oxide gives a red one. Nevertheless it will be obvious from our foregoing observations that it is possible to establish a connexion between density and colour as due to structural absorp-

* Philosophical Transactions, vol. lv. p. 10.

tion. Not, however, until we have made out a special relation can we well proceed with certainty to establish a comparative one; nor will this special relation accord with Newton's prediction.

From the nature of metachromatism, it is probable that increase or decrease of interatomic distance will in most cases be accompanied by a corresponding alteration of molecular interspaces. Hence in allotropes we shall look for exactly the opposite of what Delaval sought to establish, viz. for cold colours with great density and warm ones with low density.

Metachromatic scale.	Carbon.	Sulphur.	Topaz.	Titanic oxide.	Zircon.	Argentio iodide.	Calcic fluoride.
Black	Graphite, 2.35						
Brown	Ductile, 1.957	Brookite, 4.085	Brown, 4.515		
Red	Pink, 3.533	Dark red, 5.406	
Orange							
Yellow	Octahedral, 2.05	Yellow, 3.539	Rutile, 4.283	Yellowish green, 5.681.	
Green.....							
Blue	Blue, 3.170
White or Colourless }	Diamond, 3.33	White, 4.540	White, 3.176

The fact of phosphorus being an exception does not militate against this relation, since it is highly probable that the other anomalies of this body will receive elucidation when studied from the metachromatic standpoint. The change in colour of mercuric iodide, which we have already referred to, indicates atomic approach; and to ascertain whether this is accompanied by a corresponding molecular motion and consequent change of density has been the object of a large number of experiments. From the peculiar difficulties encountered, however, as yet I have obtained no trustworthy results.

The next step from the special relation we have pointed out to one of a comparative nature would seem to be in an extension of the following law of colour-sequence:—"In a series of anhydrous binary compounds of the same two elements, those which have the highest amount of the basylous element exhibit the

least structural absorption; and, *vice versâ*, those which have the least amount of the basylous element have the most structural absorption”*.

The Five Orders of Spectra.—In the borderland between chemistry and physics, data are being accumulated which tend to make the former a dynamical science. Not the least important of these data are those which furnish us with the connexion between the different kinds of spectra. Professor Roscoe is of opinion† that there is not sufficient evidence as yet to support the sequence in the five orders proposed by Lockyer‡ and now generally received; and in the light of metachromatism it may be necessary to modify this sequence. The juxtaposition of the orders constituting a class of spectra we take to be founded upon that merging of the optical characters of one order into those of another which is exhibited when the molecular changes in the radiating or absorbing body cause such optical alterations. Now confining our attention to low-temperature or absorption spectra, it is evident from what has already been said that change in structural absorption alone is available for forming a sequence of orders. Hence we consider the fifth order, as at present received, misplaced, the *unique continuous absorption* being from the nature of the experiment a transverse absorptional effect.

A sequence of orders will readily suggest itself if we keep in mind that change in absorption to which metachromatism is due. Conceive of a colourless body capable of undergoing the whole series of change. It first reflects or transmits rays of every refrangibility; as absorption increases, the band of transmitted or reflected light gradually narrows and becomes less intense; finally the field is darkened and we get continuous absorption. What we propose, then, is shown in the following comparison, made in order that the student may have a clearer conception of the matter.

* Chemical News, vol. xxxiv. p. 76.

† Watts's Dictionary, 2nd Supplement, p. 1093.

‡ Proceedings of the Royal Society, June 11, 1874.

Now received.		What we propose.
1st order	Line spectra	Class I. Radiative.
2nd order	Channelled-space spectra }	
		Class II.
		Absorptive.
3rd order	Continuous absorption at the blue end.....	1. Continuous absorption. 2. Partial absorption, <i>i. e.</i> absorption at the blue and red ends, or at any intermediate part of the spectrum.
4th order	Continuous absorption at the red end	
5th order	Unique continuous absorption	3. Continuous spectrum.

Class II. 1, 2, and 3 constitute the metachromatic scale. To illustrate the bridging over of 1 and 2 no simpler experiment could be tried than the following. Take a piece of copper wire and cover with suboxide by gently heating over a Bunsen burner. Fuse the covered wire into a capillary glass tube. A scarlet glass is thus obtained which is black whilst hot, *i. e.* exhibits continuous absorption (1), and scarlet whilst cold, exhibiting partial absorption (2). 2 and 3 are bridged over by a host of bodies like ZnO. When hot they, as a rule, exhibit absorption at the blue end of the spectrum (2), but when cold they are white or colourless (3).

Respecting the merging of Class I. into Class II. nothing much at present can be said, since questions are involved which require further investigation.

IX. *On a Mechanical Illustration of Thermo-electric Phenomena.* By OLIVER J. LODGE, B.Sc.

[With a Plate.]

THE publication of the following speculation requires an apology. It is in continuation of a paper on a Mechanical Illustration of Electric Induction and Conduction, published in the November Number of the 'Philosophical Magazine;' and the sections are numbered on continuously with those in that paper; but whereas the mechanical analogies suggested in the former part of the paper are useful as mere analogies even if they do not (as I believe they do) throw some light on the actual molecular processes, the present portion contains nothing of sufficient mechanical simplicity to be of much service as mere illustration, and it therefore has little value unless the imaginary

mechanical actions are really analogous to those which actually do produce thermo-electric currents. I have accordingly laid it aside for a couple of months to see if any thing would occur to show the improbability of this being the case; but as any fresh light has appeared rather to confirm than to weaken the hypothesis, I now venture to publish it. But it is necessary to say that, though the hypothesis does, with the help of a few more or less reasonable assumptions, account for all the known phenomena of thermo-electricity, yet it is quite possible that the assumptions made are not the most likely ones, and that the laws deduced are not exactly the true ones. Nevertheless, since they fulfil the necessary conditions as well as the true ones, they are sufficient to show that a consistent account of the facts can be given by means of a hypothesis founded on a connexion between the molecules of matter and electricity which is called "resistance" and which is known to exist, though it is not yet accounted for.

I have preferred to continue speaking in terms of the mechanical model, because discussions concerning molecules and æther are apt to have in appearance the looseness which they very often possess in reality. Moreover one has the advantage of being able to leave the precise relation which the cord is to bear to electricity or to the æther, and which the buttons are to bear to molecules, as well as the real nature of the connexion between the buttons and the cord, unspecified and open to any definition which the vortex theory of matter may suggest.

§ 21. In a communication to the 'Philosophical Magazine' for November 1876 (p. 353), the passage of electricity through dielectrics and electrolytes was illustrated by mechanical analogies at some length, but its passage through ordinary metallic conductors (§ 11) was only touched upon sufficiently to enable them to be compared with the other media, and all the details of the process were left unconsidered. In the present paper it is intended to enter into these details; and it is to be regarded as a continuation of the first paper.

The electrical resistance of a metal was represented by the friction to which a cord was subject in passing through a row of nearly smooth buttons fixed to a rigid support (see fig. 3, Plate II.). The cord when moving represented a current of electricity; and the buttons represented the molecules of the

conductor. But, since we were not supposing the conductor to be at the absolute zero of temperature, the buttons properly ought not to have been standing still but to have been executing some kind of periodic motion.

Let us then suppose that the rods supporting the buttons are not perfectly rigid, but highly elastic, and that each button is vibrating backwards and forwards in the direction of the length of the cord with a succession of harmonic motions of short period and very small amplitude. Each button will by its friction tend to move the cord with it. Being all exactly alike, their vibrations will all be isochronous; but they will be in all manner of phases at any one instant; so on the average they will neutralize each other's effect on the cord, and the cord will remain stationary without oscillation.

The hypothesis just made, viz. that the molecules of a solid are oscillating, and that the oscillation of any one exerts a certain electromotive force, capable of producing a current except for the circumstance that it is exerted equally in opposite directions in rapid succession, and moreover that it is in general neutralized by the similar but ill-timed action of its neighbours, is the hypothesis whose consequences it is the object of the present paper to trace.

§ 22. First of all, then, there is some energy lost in this motion; for the buttons are sliding backwards and forwards on the cord, and, though they are tolerably smooth, the friction must ultimately bring them to rest, unless the loss of energy is made up to the body from other portions of the same body or from external sources. The energy which is thus continually being wasted in warming the cord must, I think, be held to correspond to the heat lost by radiation into space; the loss being compensated, in cases of equilibrium of temperature, by equivalent receipts from neighbouring bodies. But if a set of molecules, or a finite mass of any substance, be isolated from all other bodies and left to itself in free space, the molecules will gradually deliver up their motion to the interpenetrating medium, and will ultimately come to rest. If, then, we calculate the work done in unit time by a button sliding to and fro on the cord, we shall get the rate at which a body cools under these circumstances; and from this the rate under any other circumstances can be obtained at once by simply subtracting the rate at which it gains heat from the enclosure.

Since we have no data regarding the actual motion of a button, we may as well for the present consider it as simply harmonic; any other sort of motion will give very nearly the same result. Let the period of the simple harmonic motion of a button be $2t = \frac{2\pi}{\sqrt{\kappa}}$, and let its amplitude be a , so that $2a$ is the whole length of a button's excursion from right to left. Its velocity at any distance x from its mean position is $v = \sqrt{\kappa(a^2 - x^2)}$, and its maximum velocity is $V = a\sqrt{\kappa}$. Now we remember that the retarding force acting between a button and the cord is proportional to r the specific resistance of the substance or the coefficient of "friction," and to v the velocity of the button on the cord at any instant (this is Ohm's law; see § 9 equation (1) and § 10); hence the work done in one excursion from right to left is

$$W = \int_{-a}^{+a} r v dx = \frac{\pi}{2} r a^2 \sqrt{\kappa}.$$

The work done in unit time is therefore

$$\frac{W}{t} = \frac{1}{2} r a^2 \kappa = \frac{1}{2} r V^2; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this is the rate* at which a button loses its energy when left to itself without assistance from others, or the rate of cooling of a substance placed in an enclosure at absolute zero. Hence, assuming that the absolute temperature θ is connected with the maximum velocity V and the atomic weight m by the relation

$$\frac{1}{2} m V^2 = s \theta,$$

the rate of cooling is given as

$$\dot{\theta} = \frac{s}{Jm} r \theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which would be simply proportional to θ (Newton's law), except that the resistance r itself varies with the temperature.

§ 23. The above conclusion that the radiating power of a

* If, instead of assuming a simple harmonic motion, one takes any motion having average velocity $\frac{2}{\pi} V$, the rate of doing work will be nearly $\frac{4}{\pi^2} r V^2$, which is only slightly different from (1).

body is directly proportional to its specific electrical resistance and inversely as its atomic weight, is not negatived by the experiments of Leslie, and of Provostaye and Desains, as far as they go; for Leslie's order of the metals in radiating-power agrees nearly with their inverse order in conductivity. Moreover, if one finds the value of the expression $\frac{m\theta}{r\theta}$ for the few metals more

accurately experimented on by Provostaye and Desains, one gets a number whose constancy is indeed rough but quite as good as could be expected. The only metals apparently whose radiating-powers were ascertained by them were platinum, copper, gold, and silver; and of these gold was only tried as gold-leaf, which is scarcely a fair test, because radiation is more than a surface action. The following Table contains in the first column a mean value of the radiating-power, taken from Ganot, art. 364, for the three metals, silver, copper, and platinum (gold is left out because its results are discordant); the second column contains the relative atomic weights; the third column an approximation to the relative electric conductivity of each metal, obtained by taking a mean between the value given by Matthiessen and that given by Becquerel (Miller, vol. i., being my authority); and the last column contains the numbers which ought to be constant.

	$\dot{\theta} : \theta.$	$m.$	$\frac{1}{r}$	$\frac{m\dot{\theta}}{10r\theta}$
Silver	2.7	108	100	2916
Copper	4.9	63.5	96	2987
Platinum	10.1	197	13	2586
Gold	4.3	196	71	5985

Taking 2850 as a rough mean value of this constant, one can calculate backwards to the radiating-power for any metal on the same scale. The following Table contains the radiating-power given by the hypothesis for a dozen common metals, most of whose resistances at 0° Centigrade were ascertained by both Matthiessen and Becquerel. The exclamatory mark against gold signifies that its atomic weight has been called 98 because the correct value 196 gives 2.0, which is apparently too small a result.

Metal.	Mean conduc- tivity at 0° C.	Radiating- power at zero Centigrade.
Silver	100	2.6
Gold!	71	4.1
Copper	96	4.7
Cadmium	24.1	10.6
Platinum	13	11.1
Zinc	26.5	16.5
Lead	8.3	16.6
Tin	13.2	18.3
Iron	14.6	34.8
Antimony	4.6	50.8
Mercury.....	1.7	83.8
Bismuth.....	1.25	108.6

Concerning this Table, I have to remark that the hypothesis cannot be expected to give correct values for the last three metals; for the electrical resistance was ascertained by experiment on large masses of material, whereas it is the *molecular* resistance which is concerned in radiation; and though the two are the same in homogeneous material, the experimental value of the resistance is probably too great in the case of crystalline metals like antimony and bismuth, or even perhaps iron. And as regards mercury, its molecular motions cannot be all oscillatory like those assumed in the hypothesis, but must have much of their energy in the form of whatever motion is characteristic of liquidity.

§ 24. Now the researches of Dulong and Petit have indicated the true law of cooling to be

$$\dot{\theta} = p(a^{\theta} - 1), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p is a constant depending on the nature of the substance, and a is a number usually stated to apply to all substances and to be equal to 1.0077. As, however, this is only an experimental number, I shall take the liberty of assuming that in general both p and a vary with the substance, but that the value of a is always very close to unity.

Equations (2) and (3) combined give us the law according to which the electrical resistance of a body varies with the absolute temperature, viz.:—

$$r = \frac{Jmp}{s} \cdot \frac{a^{\theta} - 1}{\theta}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

I shall denote the constant $\frac{Jmp}{s}$ by the letter h for shortness, and shall occasionally use (4) in the expanded form—

$$r = \alpha + \beta\theta + \gamma\theta^2 + \dots, \quad (5)$$

where

$$\alpha = h \log a, \quad \beta = h \frac{(\log a)^2}{2!}, \quad \gamma = h \frac{(\log a)^3}{3!}, \quad \&c.$$

The series is very converging, because a is so near 1; thus if $a = 1.0077$, $\log_e a = .0076$; and the first two terms will in many cases suffice.

Digression.

§ 25. In Balfour Stewart's 'Heat,' page 207, it is shown from the theory of exchanges that the internal radiative power of a transparent substance is proportional to the square of its index of refraction, because a small cone of rays issuing normally from some small area inside the body will spread out at the surface into a cone of larger angle, the ratio between the two solid angles being obviously μ^2 , so that to maintain equilibrium of temperature the internal radiative power must be μ^2 times that of the surface of the enclosure exposed to the plane surface of the body. There is no ground for denying an index of refraction to metals (cf. Professor Ketteler in the November Number of the 'Philosophical Magazine,' p. 333); so we will suppose the same to hold good with them.

Again, the velocity of light in a medium (*other things being equal*) will be proportional to the square root of the elasticity of the threads joining the buttons (§§ 8 and 18); for the maximum velocity V of a particle is $a\sqrt{\kappa}$ (§ 22); and this is related to the velocity of propagation of light L by the equation

$$V : L = 2\pi a : \lambda,$$

λ being of course the wave-length, whence

$$L = \frac{\lambda\sqrt{\kappa}}{2\pi}.$$

But the velocity of light in a medium is known to be inversely as μ ; therefore

$$\mu^2 \propto \frac{1}{\kappa} \propto K, \quad (6)$$

(see § 8), which appears to agree with Maxwell's theory that the index of refraction of a substance is nearly equal to the square root of its specific inductive capacity K .

We have found, then, that the internal radiating-power, which we have shown to be proportional to r , is also inversely proportional to κ , because directly proportional to μ^2 ; hence

$$\kappa \propto r^{-1}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or conductivity for heat and electric conductivity in metals are proportional to one another (for we saw in § 18 that κ was probably proportional to the conductivity for heat); and therefore the conductivity for heat varies with the temperature according to the law

$$\kappa = \frac{g}{h} \cdot \frac{\theta}{a^\theta - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which is a curve not very different from $\frac{1}{\theta}$. It vanishes for $\theta=\infty$, and it becomes great and equal to $\frac{g}{h \log a}$ for $\theta=0$.

The law of the steady conduction of heat parallel to the axis of x through a slab is

$$\frac{dQ}{dt} + \kappa \frac{d\theta}{dx} = 0.$$

Now Professor Tait, in his 'Recent Advances in Physical Science,' p. 271, says that when every thing has attained a permanent condition, the available energy would have a minimum (and therefore a stable) distribution if the temperature fell along a logarithmic curve, or if $\frac{d\theta}{dx} \propto \theta$; it is therefore to be assumed that this is the

case. But from this it follows, since $\frac{d\theta}{dt}=0$, that the *thermo-*
metric conductivity $\frac{\kappa}{\sigma}$ must vary inversely as the absolute tem-
perature. κ by itself nearly does, but not quite, (8); so we get
a law for the variation of specific heat per unit volume with
temperature, viz.

$$\sigma \propto p \kappa \theta = \frac{H}{m} \cdot \frac{\theta^2}{a^\theta - 1} \dots \dots \dots (9)$$

This is tolerably constant, or the curve runs almost parallel to the axis of θ , for ordinary ranges of temperature; it attains a

maximum about when $\theta = \frac{2}{\log a}$, and it has points of inflexion about when $\theta = \frac{2 \pm \sqrt{2}}{\log a}$, the three temperatures referred to being $-196^{\circ}4$, $-10^{\circ}8$, $+174^{\circ}8$ Centigrade, if the value of a were 1.0077 ; but a very small change in a would obviously cause great alteration in these temperatures.

One may write a tolerably close approximation to σ for ordinary values of θ thus:

$$\sigma \doteq \frac{6H}{m(\log a)^2} \cdot \frac{1}{(3 + \theta \log a)} \quad \dots \quad (10)$$

I have put p into (9) with no other justification than to get rid of it from κ (whose h contains it) so as to leave nothing but the atomic weight m in (9), except a universal constant H , this H being proportional to $m\sigma$, the atomic heat.

§ 26. In saying, as we did in § 21, that the cord remains stationary under the combined oscillatory motions of the buttons, we have assumed that the friction of a button is symmetrical as regards right and left; that is, we have assumed that the buttons are not notched so as to be rougher when sliding over the cord one way than when sliding the other way, as an ear of rye-grass would be. If this condition were not satisfied, the simple to-and-fro oscillations of the buttons would confer a progressive motion on the cord. Possibly the condition is not satisfied in some crystalline bodies, like tourmaline: and this would account for their internal polarity; for since the crystal is an insulator, the cord will be displaced by the unequal friction only so far as the dielectric elasticity will permit it, and the result will be a state of strain inside the crystal and a difference of potential between its opposite faces. In time the potentials of these faces would become equalized by surface leakage or otherwise; but any quickening of the motions of the molecules (rise of temperature) will increase the electric displacement and strain, and will restore a certain amount of difference of potential to the faces. On the other hand, a lowering of the temperature of the crystal will give the elasticity an advantage over the friction; some of the previously displaced cord will return, and the potentials of the faces will change sign.

§ 27. Return now to the consideration of a simple metallic conductor with its buttons all executing isochronous simple harmonic motions on the cord. Apply a force to the cord so as to make it move continuously forward with a velocity u ; that is, generate a current of strength proportional to u in the conductor by means of external electromotive force. We will not suppose that u is great enough at all to interfere with the motion of the buttons; in other words, we will assume that u is incomparably less than V ; nevertheless the vibrations of the buttons, though unaltered in space, are no longer symmetrical right and left with respect to the cord: in one direction their relative velocity is the sum, in the other the difference of their respective velocities; hence the motion of the cord is resisted, and work must be done to drive it. If the buttons were stationary, the force opposing the motion of the cord in each button would be ru by Ohm's law; and this force is unaltered by the motion of the buttons so long as u is small. For consider the work done by a button in one excursion; properly speaking it would be

$$W = \int_{-(a \pm \frac{1}{2}ut)}^{a \pm \frac{1}{2}ut} (v \pm u) r dx, \quad (11)$$

the signs to be taken according as the excursion is against or with the cord; but as this expression is unmanageably long, I will be content with the simpler one, true when u is small,

$$W_1 = \int_{-a}^{+a} (v + u) r dx = \frac{\pi}{2} r a^2 \sqrt{\kappa} + 2aru$$

for the work done by a button in an excursion against the cord, and

$$W_2 = \int_{-a}^{+a} (v - u) r dx = \frac{\pi}{2} r a^2 \sqrt{\kappa} - 2aru$$

for the work done in an excursion with it. The balance of work done against the cord in a double excursion (that is, while the button travels over a distance $4a$) is

$$W_1 - W_2 = 4aru; \quad (12)$$

hence the average force exerted must be equal to ru .

The rate of *radiation* work of a button is

$$\frac{W_1 + W_2}{2t} = \frac{1}{2} r a^2 \kappa, \quad (13)$$

the same as that given by equation (1) when no current was passing.

We have found, then, that each button exerts an average force on the cord equal to ru ; hence, if there are n buttons in a row on each cord, and m cords lying side by side, the electromotive force or difference of potential required to drive a current of strength $mu=C$ through a conductor of sectional area represented by m , and length represented by n , is

$$\frac{F}{m} = E = nru = \frac{n}{m} r \cdot mu = RC, \quad . \quad . \quad . \quad (14)$$

which merely shows that Ohm's law, if true for each button, is true for the whole conductor if its temperature is kept constant. The work done by this force in any time T will be equal to the product of the force into the distance through which it may have moved the cord in that time—that is, FuT ; hence the rate of “frictional” generation of heat by the current is

$$jmnru^2 = jRC^2, \quad . \quad . \quad . \quad . \quad (15)$$

which is Joule's law that the amount of heat generated in a given time is proportional to the resistance of the conductor and to the square of the strength of the current. It is convenient to use j for the number of units of heat contained in a unit of work, *i. e.* for the reciprocal of J .

Though I have here taken account of more cords than one, it will not be necessary to do this hereafter, as what is true for any one cord will be true for any number, so we will henceforth consider $m=1$.

§ 28. So far we have considered only homogeneous circuits, in which all the buttons have the same amplitude, the same period, and the same average velocities. In these cases the cord is in equilibrium under the united and balanced action of all the buttons on it, but it is perfectly free and capable of permanent displacement by the slightest force; so that if even one button were made to move forward always faster than it returned, it would exert an electromotive force on the cord and move it forward a little at each oscillation. On the other hand, if any button be made to go forward more *slowly* than it returns, it will exert less force on the cord than is expected of it, and the cord will be moved backwards by the other buttons while the slow one is going forward. Hence if we con-

ceive a cord on which all the buttons but one are oscillating regularly to and fro with the average velocity v , while this one is oscillating forwards with velocity $v+x$ and backwards with velocity $v-x$, then the cord will be pushed forward *both* by reason of the too rapid motion and by reason of the too sluggish one; and the electromotive force urging it is

$$(v+x)r-(v-x)r=2xr. \quad . \quad . \quad . \quad (16)$$

If the cord were allowed to move, the work done per second by this force would be $2xru$; and j times this is therefore the rate at which heat is absorbed at such a point by this force. The heat so absorbed is evolved in other parts of the circuit, because friction opposes the motion of the cord with a force *nur* equal to $2xr$. If we urge the cord at any rate u through such a circuit by an external electromotive force E acting in the same direction as the force of the x -button, the work done per second is

$$Eu=(nur-2xr)u,$$

or the heat generated is

$$j(nu^2r-2xru), \quad . \quad . \quad . \quad . \quad (17)$$

and the strength of the current is

$$u=\frac{E+2xr}{nr}=\frac{E+\Pi}{R}. \quad . \quad . \quad . \quad (18)$$

Now (17) contains two terms, one depending on the square of the current and being the irreversible frictional generation of heat (15), and the other changing sign with the current and representing the heat absorbed or generated at the x -button according as u is positive or negative, remembering that the current has been considered positive when going the way the button tends to drive it.

Something analogous to the unsymmetrical action of this x -button is what I imagine to go on at a junction either of two different metals at the same temperature, or of two parts of the same metal at different temperatures; and accordingly $2jxru$ will correspond either to the Peltier effect or to Thomson's *convection* effect; and $2xr$ is analogous to the coefficient which is called Π in the one case and may be called Θ in the other.

§ 29. Let us now proceed to consider what kind of unsymmetrical motions may reasonably be expected to actually occur at a junction either of two different metals at the same tempe-

ture, or of two portions of the same metal at different temperatures. In both cases the molecules on the two sides of the junction are vibrating at different rates:—in the first case so that

$$m_a v_a^2 = m_b v_b^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

m_a and m_b being the atomic weight of the two metals; and in the second case so that

$$\theta_2 v_1^2 = \theta_1 v_2^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

θ_1 and θ_2 being the absolute temperature on either side of the junction.

Now it is very unlikely that the vibrations of the closely packed molecules of a solid should be any thing so simple as the simple harmonic motions partially assumed in §§ 22 and 27: in other words, the restoring force cannot be due simply to bending of the connecting rods, but it must also be an effect of the neighbouring buttons by impact or otherwise. Any button in the interior of a mass of metal will be driven backwards and forwards with a velocity depending on the average velocities of the buttons in its neighbourhood as well as on the elasticity of its connecting rods; and if the mass be homogeneous, its velocities to right and left will be equal. But consider a button on the bounding surface of a mass in vacuum. It is being struck behind continually by its contiguous buttons, but there is nothing striking it in front; and accordingly its velocity in the excursion outwards will be greater than in its return journey, the return having to be accomplished by the strained rods in opposition to the force of impact. Any cause which either increases the average velocity of the molecules or decreases the elasticity of the rods will increase the difference between the out and in velocities, which may be said to depend on v directly and on $\sqrt{\kappa}$ inversely. Now a rise of temperature does both these things; it increases v in proportion to $\sqrt{\theta}$, and it decreases κ in the proportion of $\frac{1}{\theta}$ (see (8)); hence the difference of velocity may without violence be assumed to be simply proportional to the absolute temperature in any given medium. As the temperature rises, then, a surface molecule will go forward more and more rapidly and return more and more slowly;

moreover its mean position will be shifted more and more outwards: occasionally a molecule may get struck away altogether, which is evaporation.

If we bring a second mass of the same material at the same temperature into close contact with the first mass, the surface-buttons of each will drive one another inwards, and they will oscillate like any other buttons in the interior of a homogeneous mass. But if the second mass of metal be either of different material or of different temperature from the first mass, its molecules will not be oscillating at the same rate; and though the surface-buttons of each will be partially restored to their places and made to oscillate more uniformly than before, yet, since the impacts of one are more violent than those of the other, they will still have some irregularity—those of the hotter metal A going faster from A towards B and slower in the reverse direction, while those of B go slowly from B to A and faster back again from A to B. On the whole, then, we have a *double* layer of buttons oscillating quicker in one direction, viz. A B, than the other*; and such buttons, if threaded on a cord, would have a tendency to drive it in the direction A B, as we have already seen, § 28.

§ 30. At a junction of two metals, or of unequally hot pieces of one metal, we appear then to have found an electromotive force acting in one direction; but there is something

* Although we should have at such a junction molecules travelling quicker in one direction than the other, there will be no excess of momentum either way as was to be expected in dielectrics and electrolytes (see § 8 footnote and § 16); for there will be a large number of molecules side by side in such a layer, and, since each takes a longer time over its slow journey than over its quick one, there will be at any instant more molecules moving slowly than quickly, and their excess in number will make up for their defect in velocity, so that the average momentum each way will be the same. But it is a suggestion of Mr. G. Johnstone Stoney's, which he made at the Physical Society last November, in connexion with his theory of Mr. Crookes's radiometer, that though mv may equal $m'v'$ it by no means follows that $\frac{1}{2}mv^2 = \frac{1}{2}m'v'^2$: there will, in fact, in the above arrangement be an excess of kinetic energy in favour of the quickly moving molecules, *i. e.* from A to B. This is energy which can be expended in driving the cord. But if the cord be forcibly held so that it cannot move, the energy will still, I suppose, be transferred from A to B; but it will not now be doing useful work, it will be degraded into mere diffusion of heat.

further to be noticed yet. We found in the former paper that in any complete model it was necessary to have not one cord but two, arranged side by side and connected so that however one moves the other must move with the same velocity in the opposite direction—one representing a current of positive, the other the simultaneous equal opposite current of negative electricity. Now the electromotive force whose existence we have been recently imagining, is one that will act on both these cords ; and if it acted on both equally they would be both urged equally in the same direction, and consequently could not move at all. It is necessary, therefore, to assume that the bite of the buttons on one of these cords is greater than their bite on the other ; but whether it is the positive or the negative cord on which the greatest force is exerted in a given case will depend on the nature of the metal, and possibly also on its temperature—though we have no evidence as regards the latter point, and I shall not assume it.

What we have now assumed amounts to this, that the quantity r , called the specific resistance of a substance, is made up of two parts, such that $r = r' + r''$, whereof r' is the specific resistance referred to positive electricity, and r'' is the specific resistance referred to negative electricity, and that in any metal in which a current exhibits *convective power for heat* the two parts are not equal. If the “specific heat of vitreous electricity” is positive (as Thomson has experimentally proved it to be in copper), r'' is greater than r' ; but if it is negative (as it is in iron), then r' is greater than r'' . However, this will appear more fully presently, § 35.

§ 31. Consider now the electrical condition of a homogeneous mass of metal. Its surface molecules are moving more quickly outwards than inwards, and are hence straining the cords outwards (which cord they strain most depends upon circumstances ; but for simplicity I will suppose that there is only one, and that the positive cord): the cord inside is thus in a slight state of tension, or (§ 1) the potential of the metal is lower than that of the air in its neighbourhood. The cord does not move, because the surface forces are balanced all round : it resembles a drop of water in a capillary tube. (If the negative cord were acted on most, the condition of the metal would resemble mercury in a capillary tube, or simply

a drop of water in its own skin.) Another mass of different material will show the same thing, only to a different amount. If the two metals are put into contact, we have three kinds of bounding surfaces, viz. those which separate air and A, A and B, B and air; and the forces at each surface are in general different: hence the forces all round A are no longer balanced, and the cord moves, say from A to B, a certain limited extent, just as the water in two capillary tubes of different bore would when they are brought into contact. The particles of the dielectric outside (being also threaded on the cord) will at the same time be pulled nearer to A and pushed further from B; that is, §§ 1 and 2, the surface of A is charged negatively and that of B positively.

§ 32. The difference of potential produced by the above surface-action is closely allied to Volta's contact electricity, which is also an effect taking place at the free surfaces of the two metals, but which is probably greatly assisted by an incipient voltaic current taking place through the air which acts as the exciting fluid, the electromotive force being produced by the tendency of the air to unequal chemical action on the two metals. Since the air is a dielectric and not an electrolyte, there is no continuous current developed, but only a difference of potential capable of causing a current if the resistance of the air were diminished sufficiently; and the cord is displaced through the air and across the junction of the two metals to an extent proportional to this difference of potential, the electromotive force being balanced by the slight state of strain which is set up in the air by this displacement. The metals which show the greatest effect are those which stand furthest apart in the voltaic series.

But the contact electricity spoken of above as generated at the junction of two metals has nothing to do with chemical action. It is an incipient thermo-electric current taking place across the junction, which only shows itself as a slight displacement of the cord, unless the metallic circuit is completed by a second junction generating an electromotive force different from that of the first. The action between zinc and copper would not be at all so strong as between bismuth and antimony: in fact, the metals stand here in their thermo-electric order. Of course, what is actually observed in any

ordinary case of two metals in contact is a mixture of the two effects ; and the voltaic effect is usually far the greatest.

§ 33. The very provisional value $2\pi r$ already obtained in § 28 for the electromotive force at a junction is sufficient to show several things. For instance, since it is a direct function of resistance, substances of high specific resistances may be expected to make the best thermo-electric materials—such, for example, as metallic alloys, or sulphides, or, still better, tellurium or selenium*. Hence also we might expect contact effects to be extremely powerful between two substances ordinarily called “insulators.” Some violence might have to be used to displace the cord through the very rough buttons of a dielectric ; and a certain amount of heat would be generated by the “friction” of the cord through the buttons ; but when once displaced it would not easily slide back again, and the effects might accumulate ; so that by rubbing a dielectric with a cord-supplying substance (a metal), one could electrify it very highly ; and this is done in an ordinary glass electrical machine. Any two substances which differ at all in conducting power may be expected to give some contact-force. Thus, if a crystalline metal conducts better along the fibre than across, or if a strained metal has a higher resistance than an unstrained, or if the conductivity of magnetized iron depends on the direction of magnetization, then contact-force may be looked for in each case at the junction of the substance in its two different states.

§ 34. It is now time to try what are the actual values which the assumptions founded on the model give for the electromotive force developed at junctions, and to see if these values satisfy the conditions which Thomson has laid down for them from thermodynamic principles. Consider, therefore, a junction of two metals A and B, at the temperature θ , whose resistances are r_a and r_b , such that r'_a and r''_a are the positive and negative resistances respectively of the metal A (referring to § 30 for an explanation of these terms), and r'_b , r''_b of B ; also let v_a and v'_a be the out and in velocities (§ 29) of the

* Since the resistance of selenium has been found to fall off under exposure to light, it is probable that its “thermo-electric power” will be found to do so also ; in other words, illuminated selenium will have a place higher up in the thermo-electric series than unilluminated selenium.

molecules of the metal A, and v_b and v'_b those of the metal B: then the force exerted on the positive cord is

$$F = (v_a - v'_a)r'_a - (v_b - v'_b)r'_b. \quad . \quad . \quad . \quad (21)$$

Now in § 29 we agreed to consider the difference of the out and in velocities to be proportional to the absolute temperature in any particular metal*: hence we shall have

$$F = A\theta r'_a - B\theta r'_b;$$

similarly for the force acting on the negative cord we shall have

$$F' = A\theta r''_a - B\theta r''_b.$$

Hence the balance of force useful for urging the cords is

$$\Pi = F - F' = \theta \{ A(r'_a - r''_a) - B(r'_b - r''_b) \}. \quad . \quad (22)$$

Now (§ 24) r is of the form $h \frac{a^\theta - 1}{\theta}$; and from what was said in § 30 it is plain that h must not only vary for different substances, but must have in general different values for the positive and negative cord in any one substance. Call these values h' and h'' , so that $h = h' + h''$. h also changes from one substance to another, and so does a ; but I shall assume that the latter is constant as regards the positive and negative cords; if, however, the sign of the specific heat of electricity in a substance were found to depend upon the temperature, then a must also be split into two parts a' and a'' . At present I shall only assume that it is different in A and B, and shall call its value in B, b . Putting the values of r into (22), we get

$$\Pi = A(h'_a - h''_a)(a^\theta - 1) - B(h'_b - h''_b)(b^\theta - 1). \quad . \quad (23)$$

This is the electromotive force generated at a junction of two

* The account given in § 29 of the cause of the difference between the out and in velocities at a junction cannot be held to apply satisfactorily to the case of a junction of two different metals; for it makes the thermo-electric power of a metal to depend on the substance with which it is associated, instead of being a simple property of each individual metal and its temperature—as it is known to be, because the metals can be arranged in a thermo-electric series at any temperature. Hence, whatever influence difference of atomic weight may have in producing the unsymmetrical action very reasonably to be expected at a junction, it cannot act quite in the manner suggested in § 29; for the difference between the out and in velocities of any particular substance must really depend only on its own physical properties, and not on those of the substance with which it is put into contact.

Now (4)

$$dr = h \frac{\theta a^\theta \log a - a^\theta + 1}{\theta^2} d\theta;$$

hence, integrating,

$$\Theta = \int_{\theta_2}^{\theta_1} d\Theta = A(h' - h'') \left\{ \alpha^{\theta_1} - \alpha^{\theta_2} - \int_{\theta_2}^{\theta_1} \frac{\alpha^\theta - 1}{\theta} d\theta \right\}, \quad (27)$$

a force acting in the direction from hot to cold when $h' - h''$ is positive.

This, then, is the coefficient of Thomson's effect; or if a current of strength u be sent through the metal in opposition to the above force, the heat generated per second is (§ 28)

$$j^{\Theta}u, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

which will show itself as a convection of heat by the current in one direction or the other, according as h' is greater or less than h'' . Thus, if the current *generates* heat or “carries heat with it” in passing through the metal from hot to cold, the electromotive force \ominus must be acting from cold to hot; and therefore the bite of the buttons on the negative cord must be greater than on the positive, or h'' must be greater than h' . This is the case in copper. But, on the other hand, if the current *absorbs* heat in passing from hot to cold, so that the heat appears to travel *against* the current (that is, if the “specific heat of vitreous electricity” be *negative*), then the electromotive force \ominus must be acting *with* the current, or from hot to cold; that is, h' is greater than h'' , and the *positive* cord is most acted on. This is the case in iron.

The quantity of heat carried down *small* unit difference of temperature in unit time by unit positive current (that is, by unit quantity of vitreous electricity), Thomson calls ("without theory, but by an obvious analogy") *the specific heat of vitreous electricity in the substance A*, and writes it σ_a ; in other words, the reversible heat generated by forcing a current u against the force Θ from a point at a temperature θ to a point at a temperature $\theta + d\theta$ is

$$iud\Theta = -\sigma ud\theta. \quad (29)$$

The value of σ in any substance is therefore (26)

$$\sigma_a = -jA\theta \frac{dr' - dr''}{d\theta} = -jA(h'_a - h''_a)\theta \cdot \frac{d}{d\theta} \left(\frac{a^\theta - 1}{\theta} \right), \quad (30)$$

and similarly, of course, for σ_b . Hence (23) obviously follows Thomson's relation

$$\frac{d\left(\frac{\Pi}{\theta}\right)}{d\theta} + J \frac{\sigma_a - \sigma_b}{\theta} = 0. \quad [15]^*$$

§ 36. It is easy now to find the total electromotive force of a complete thermo-electric circuit—that is, the electromotive force acting in a ring made of two metals A and B, one of the junctions being at a temperature θ_1 , the other at a temperature θ_2 ; for we have simply to add the difference of the two Peltier effects to the difference of the two Thomson effects, (23) and (27), and we get

$$\begin{aligned} E = \Pi_1 - \Theta_a - \Pi_2 + \Theta_b &= A(h'_a - h''_a) \int_{\theta_2}^{\theta_1} \frac{a^\theta - 1}{\theta} d\theta \\ &\quad - B(h'_b - h''_b) \int_{\theta_2}^{\theta_1} \frac{b^\theta - 1}{\theta} d\theta, \quad (31) \end{aligned}$$

which is evidently equal to

$$\int_{\theta_2}^{\theta_1} \frac{\Pi}{\theta} d\theta, \quad [17]$$

as Thomson has shown it must be.

It is evident also from the form of Π , viz.

$$\Pi_{AB} = P_A - P_B,$$

that

$$\Pi_{AB} + \Pi_{BC} + \Pi_{CD} + \dots + \Pi_{YZ} + \Pi_{ZA} \equiv 0, \quad (32)$$

provided θ is the same for all—or that the electromotive force in a ring formed of any number of metals all at the same temperature is zero. The values found for the effects therefore satisfy all the conditions laid down for them.

§ 37. So far I have written down the results of our hypothesis without any approximation; but simpler and nearly accurate values will be obtained by expanding them all in series and taking the first term or two, or, what comes to the same thing, by using the first two terms only of the expression (5) for r . Thus, writing

* The numbers in square brackets refer to Thomson's equations so numbered in his papers on "The Dynamical Theory of Heat. Part VI.—Thermo-electric Currents," reprinted from the Trans. R. S. Edin., in the Phil. Mag. for March, April, May, and June 1856.

$r'_a \triangleq \alpha_0 + \alpha\theta$, $r''_a \triangleq \alpha'_0 + \alpha'\theta$, $r'_b \triangleq \beta_0 + \beta\theta$, $r''_b \triangleq \beta'_0 + \beta'\theta$, we get at once from the hypothesis all the results in the form given to them by Tait, and experimentally verified by him for moderate ranges of temperature. The contact-force at a junction (22) becomes

$$\Pi \triangleq \theta \{ A(\alpha_0 - \alpha'_0) - B(\beta_0 - \beta'_0) + \theta [A(\alpha - \alpha') - B(\beta - \beta')] \}, \quad (33)$$

which is of the form

$$X\theta - Y\theta^2;$$

and the neutral temperature of Cumming is

$$\theta_0 \triangleq \frac{X}{Y} = - \frac{A(\alpha_0 - \alpha'_0) - B(\beta_0 - \beta'_0)}{A(\alpha - \alpha') - B(\beta - \beta')}. \quad (34)$$

We may write for (33)

$$\Pi \triangleq Y\theta(\theta_0 - \theta), \quad (35)$$

which will be precisely Tait's form (see Maxwell, p. 306) provided $jY\theta$ comes out to be the difference of the specific heats of electricity in the two metals at the temperature θ .

To find Θ , one has from (26)

$$d\Theta_a \triangleq A\theta(\alpha - \alpha')d\theta,$$

or

$$\Theta_a \triangleq \frac{1}{2}A(\alpha - \alpha')(\theta_1^2 - \theta_2^2), \quad (36)$$

whence, from the definition of the specific heat (29),

$$\left. \begin{aligned} \sigma_a &\triangleq -jA(\alpha - \alpha')\theta, \\ \sigma_b &\triangleq -jB(\beta - \beta')\theta; \end{aligned} \right\} \quad (37)$$

and therefore, (33), the condition in (35)

$$jY\theta \triangleq \sigma_a - \sigma_b \quad (38)$$

is satisfied.

The total electromotive force in a thermo-electric circuit is obtained, either like (31) by finding $\Pi_1 - \Pi_2 - \Theta_a + \Theta_b$, or by forming the integral $\int_{\theta_2}^{\theta_1} \frac{\Pi}{\theta} d\theta$; and its value is

$$E \triangleq Y(\theta_1 - \theta_2) \{ \theta_0 - \frac{1}{2}(\theta_1 + \theta_2) \}. \quad (39)$$

The law was originally given nearly in this shape by Avenarius*; but he omitted the two Thomson effects, and consequently his formula was erroneous. The above form is that of Tait†, who has verified it for moderate ranges of temperature.

Tait also shows that if T_{ab} stand for the temperature θ_0 at which two metals A and B are neutral to one another, and

* Pogg. Ann. vol. cxix. (1863).

† Proc. R. S. Edin. 1870-71.

if σ_a be equal to $k_a\theta$ (where k is a constant), then must

$$(k_b - k_c)T_{bc} + (k_c - k_a)T_{ca} + (k_a - k_b)T_{ab} \equiv 0.$$

Now from (34) and (37)

$$(k_a - k_b)T_{ab} = A(\alpha_0 - \alpha'_0) - B(\beta_0 - \beta'_0), \quad . \quad . \quad (40)$$

and the cyclical sum of three, or of any number, of such terms evidently vanishes.

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JANUARY 20, 1877.

XII. *A Sensitive Mercury Barometer.*

By FREDERICK GUTHRIE.

THE object aimed at is to get a barometer which shall combine great sensibility with sufficient compactness. The barometers depending upon the weight of liquid columns are, unless the liquid is mercury, of unwieldy length. Descartes suggested a modification of the mercurial barometer in which the air-supported column of liquid consists of two liquids, the lower one being mercury and the upper one water holding tartar-emetic in solution to ensure the expulsion of air (fig. 1).

Now that we know various liquids, notably hydrocarbons, which have no sensible vapour-tension at atmospheric temperatures, it is surprising that this form has not been reintroduced. It appears, however, to be little known. It was suggested to me by a friend; and I made one containing glycerine and used it with success for some months before I was aware of its having been suggested by Descartes. The sensibility of such a barometer would obviously be, if the upper liquid were without weight, directly proportional to the ratio between the sectional areas of the cylindrical chamber and the upper tube (if also the open limb were of infinite area). But, the upper liquid having weight, the limit of sensibility is the comparative density of the mercury and liquid (say 16:1). Accordingly this limit is reached when the cylindrical chamber has four times the diameter of the upper tube.

Fig. 1.



By inclining the top part of the supported column a theo-

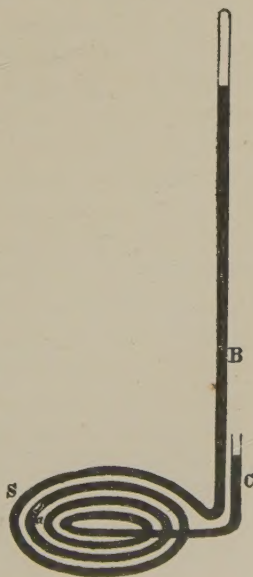
retical increase of sensibility is obtained; but practically, on account of the dragging on the column and for other reasons, this device is not in use for exact measurements. The multiplication of motion caused by applying a float connected with a wheel, as in the common weather-glass, is for similar reasons to be discarded for such purposes. Aneroid barometers are of exceedingly convenient form, but are of course saddled with the objection that the metal chamber is never perfectly elastic, so that they require frequent comparison with standard mercurial ones.

My friend the late B. F. Duppa devised a barometer in which the cistern or open limb was dispensed with, and was replaced by an open horizontal capillary tube. The free surface of the mercury in the capillary tube would then move at a rate proportional to the sectional areas of the vacuum end and the capillary. I believe this plan was not found to answer, on account of the oxidation of the free end of the mercury.

The plan which I submit, and which in the models I have made and have had made appears to succeed well, more resembles that of M. Duppa than of any other with which I am acquainted. One form, shown in fig. 2, made for me by

Fig. 2.

Messrs. Cetti, of Brooke Street, Holborn, consists of an ordinary barometer-tube, B, 6 millims. in internal diameter, connected by a flat horizontal spiral, S, of 2 millims. internal diameter, with the open tube C of the same diameter as B. In S is a bubble of air, *a*, at such a distance from B that it cannot enter B when the mercury in that tube is at the top. The motion of the bubble is, of course, 9 times as fast as that of the level of the mercury in either limb, or $4\frac{1}{2}$ that of the true barometric variation. The object of bringing B and C together is to avoid as much as possible the effect of the relative differences of height on change of place. In another form (which is being made by Mr. Hicks, of Hatton Garden), the limb



C is made to enclose hermetically the limb B. This should bring the effect of such relative tilting to a minimum. In one which I have myself made, the tube S being straight and placed on a stone mantelpiece, a drop of sulphuric acid is employed instead of the air-bubble. It has the effect of making the motion rather more nimble, but is perhaps not quite so trustworthy for exact measurements, because the wetting of the tube by the liquid causes some inconstancy in its calibre. A tube S of 2 millims. internal diameter, connected with a barometer-tube having at its upper mercurial surface a diameter of 20 millims., would exaggerate barometric motion 100 times; and of course the sensibility would approach the nearer to twice this, the greater the diameter of the open limb. There is indeed absolutely no theoretical limit to the possible sensibility. It must be left to practical glass-workers to determine whether a spiral form is the best for the tube S, or whether a series of parallel tubes joined alternately end to end are to be preferred. According to Professor Dewar, who has had great experience in the use of such tubes for similar purposes, it would not be advisable to have the S tube less than 2 millims. internal diameter. In all cases, on account of the unavoidable irregularities in so long a tube, I presume as many as possible comparisons should be made with a standard barometer and the intermediate graduations introduced by interpolation. In the straight one mentioned above, the gap in the mercury thread is seen through a lens to be in constant agitation.